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Heptamethylenediamine at 213 K

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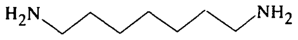
Abstract

Heptamethylenediamine, $C_7H_{18}N_2$, molecules in the crystal structure are orientated parallel to the *a* axis and aggregate side to side in successive layers parallel to the *bc* plane. The bonds within the saturated chain show small variations in their length. Two weak intermolecular N—H···N hydrogen bridges occur between the molecules of successive layers.

Comment

As part of our study on bolaamphiphilic compounds containing an aliphatic chain, we present the structure of the free base of heptamethylenediamine, (I). It can be seen from Fig. 1 that the displacement ellipsoids of the odd-numbered atoms all have the same orientation, as do the even-numbered atoms. These two different orientations are both perpendicular to the molecular axis. This, in connection with the more specific orientations of the ellipsoids (for the even-numbered atoms in the bond-angle-bisecting direction) suggests, that the molecules undergo rigid-body motions maintaining the unique direction of their axes.



(I)

The molecule has exact C_s symmetry, with the fourth C atom of the aliphatic chain being positioned on the crystallographic mirror plane. The long *a* axis of the unit cell (see Fig. 2) provides an obvious clue to the general direction of the chains. The molecules aggregate side to side in successive layers which lie parallel to the *bc* plane and are connected *via* intermolecular hydrogen bridges between the N atoms, of which one has an N···N distance of 3.220 (7) Å and an N—H···N angle of 148 (4)°. The next closest intermolecular N···N contact with the second nitrogen-bonded H atom close to it has a distance of 3.457 (5) Å. This is slightly longer than the usual limit for hydrogen bridges (Jeffrey & Saenger, 1994), but the N—H···N angle of 154 (3)° is better than the angle found for the other hydrogen bridge. Thus, every N atom is an acceptor for two hydrogen bridges which lead to the amino groups of two different molecules in the neighbouring layer. Consequently the two hydrogen bonds are weak. Previous investigations of hexamethylenediamine (Binnie & Monteath Robertson, 1950) showed an inclination of ±25° of the chains to the *a* axis, while the heptamethylenediamine chains lie parallel to the *a* axis. Since these molecules all have the same general direction, the hydrogen bridges are significantly bent. This further weakens the hydrogen bonds (Jeffrey & Saenger, 1994) and leads to a low melting point of 300 K.

For hexamethylenediamine (Binnie & Monteath Robertson, 1950) and the dihalides of heptamethylenedi-

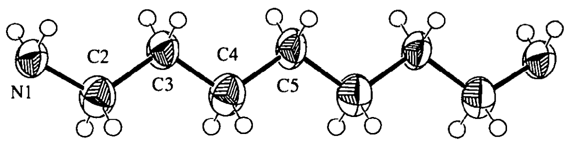


Fig. 1. *ORTEP*II (Johnson, 1976) plot of the title molecule. Displacement ellipsoids are plotted at the 50% probability level.

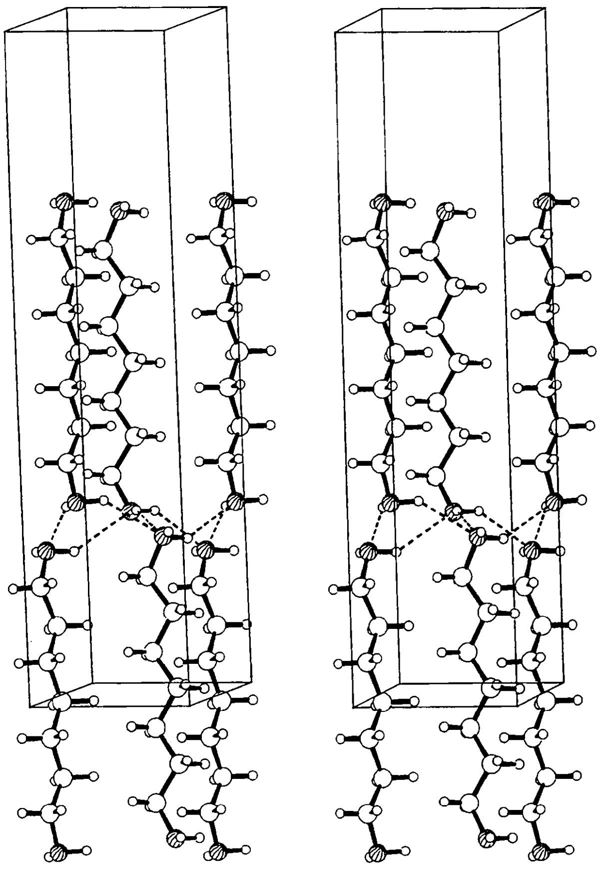


Fig. 2. Stereoview (*SCHAKAL*; Keller, 1990) of the cell of heptamethylenediamine. The dotted lines indicate the hydrogen bridges.

amine (Brisson & Beauchamp, 1988; Brisson & Brisse; 1984), a slight alternating change in bond length was observed within the saturated chain, which we also found for the title compound (see Table 2). The closest molecular packing of the parallel chains within the layer is in the diagonal directions $c+b$ and $c-b$. The planes of neighbouring molecules in these directions form an angle of 85°, which leads to a repetitive pattern for every two molecules. Since the structure of the even-chained hexamethylenediamine (Binnie & Monteath Robertson, 1950) shows the same phenomenon, it seems possible that repulsive interactions between the lone-pair electron of the nitrogen and the protons of the C atoms is responsible for this pattern.

Experimental

Heptamethylenediamine is extremely hygroscopic. Crystals, obtained from solutions such as dioxane or ethanol–propan-2-ol, are very fine and cannot be preserved in the open atmosphere. However, it was found that large crystal plates could be obtained by distillation of a 70% solution in methanol from caustic soda under reduced pressure and a stream of dry argon. The diamine distilled at 360 K under a pressure of 16 mmHg (1 mmHg ≈ 133.322 Pa). These plates were too large for accurate X-ray diffraction work, but specimens of suitable dimensions could be cut from them with a razor blade at 277 K under a dry argon atmosphere. To preserve the crystals, they were put into a small glass tube (diameter 0.5 mm, wall thickness 0.01 mm) which was sealed with plasticine. In this manner, the crystals could be kept for several weeks, enabling a full single-crystal X-ray measurement. The crystal chosen was placed in the centre of the four-circle diffractometer, then slowly cooled to 213 K with an Oxford Cryosystems N_2 gas-stream device (Cozier & Glazer, 1986) and kept at that temperature.

Crystal data

$C_7H_{18}N_2$
$M_r = 65.12$
Orthorhombic
$Cmc2_1$
$a = 22.806\,(7)$ Å
$b = 6.450\,(2)$ Å
$c = 5.813\,(2)$ Å
$V = 855.1\,(5)$ Å^3
$Z = 4$
$D_x = 1.012$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ (Ni-filtered) radiation
$\lambda = 1.54180$ Å
Cell parameters from 49 reflections
$\theta = 11.7$–$20.0°$
$\mu = 0.462$ mm^{-1}
$T = 213.0\,(2)$ K
Platelet
0.50 × 0.35 × 0.20 mm
Colourless

Data collection

Stoe four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1293 measured reflections
408 independent reflections
345 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.047$
$\theta_{\rm max} = 63.45°$
$h = -26 \rightarrow 26$
$k = -7 \rightarrow 7$
$l = 0 \rightarrow 6$
4 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.156$
$S = 1.069$
408 reflections
52 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.068P)^2 + 0.5446P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$

$\Delta\rho_{\rm max} = 0.165$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.120$ e Å^{-3}
Extinction correction: *SHELXL*
Extinction coefficient: 0.0060 (16)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = −0.7 (21)

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

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

	x	y	z	$U_{\rm eq}$
N1	0.72270 (11)	0.7030 (6)	0.4747 (9)	0.0523 (11)
C2	0.66733 (9)	0.7872 (5)	0.3962 (6)	0.0520 (12)
C3	0.61154 (9)	0.7092 (5)	0.5183 (6)	0.0480 (13)
C4	0.55592 (9)	0.7981 (5)	0.4165 (9)	0.0536 (15)
C5	1/2	0.7141 (6)	0.5291 (9)	0.049 (2)

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

N1—C2	1.448 (4)	C2—C3	1.541 (4)
N1—H11	0.85 (3)	C3—C4	1.512 (4)
N1—H12	0.94 (5)	C4—C5	1.532 (4)

The four reference reflections showed no changes other than statistical ones during the measurement. On account of the space group and radiation chosen, the number of independent reflections is rather low. Cu $K\alpha$ had to be used to avoid interference of neighbouring reflections, since the reflections are broad and the lattice constant a is long. The reflection profiles without background had a width of 1.5° and more with increasing θ by the ω–2θ scan. The ω step was 0.02° with the time of measuring between 0.3 and 2.1 s to reach $I/\sigma(I) > 30$. It was not possible to obtain crystals of better quality. They were of irregular habit with badly defined faces and edges. The linear absorption coefficient is rather low; an absorption correction was not applied. The H atoms could be located in a difference Fourier synthesis. All H-atom parameters were refined. Atoms H11 and H12, which are bonded to N1 and participate in hydrogen bridges, were refined individually. H2*A* to H5*B* were refined as H atoms coupled with *AFIX* (*SHELXL*93; Sheldrick, 1993) to the corresponding C atoms in order to reduce the number of variables.

Data collection: local program. Cell refinement: Stoe software. Data reduction: local program. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93. Molecular graphics: *ORTEP*II (Johnson, 1976) and *SCHAKAL* (Keller, 1988). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1075). Services for accessing these data are described at the back of the journal.

References

Binnie, W. P. & Monteath Robertson, J. (1950). *Acta Cryst.* **3**, 424–429.

Brisson, J. & Beauchamp, A. L. (1988). *Acta Cryst.* C**44**, 1152–1153.

Brisson, J. & Brisse, F. (1984). *Acta Cryst.* C**40**, 1402–1404.

Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Jeffrey,G. A. & Saenger,W. (1994). Monograph. *Hydrogen Bonding in Biological Structures*, pp. 18, 29. Berlin: Springer-Verlag.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Keller, E. (1988). *SCHAKAL*88. *Fortran Program for the Graphic Representation of Molecular and Crystallographic Models*. University of Freiburg, Germany.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

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3-(4-Nitroanilino)-2-cyclopenten-1-one

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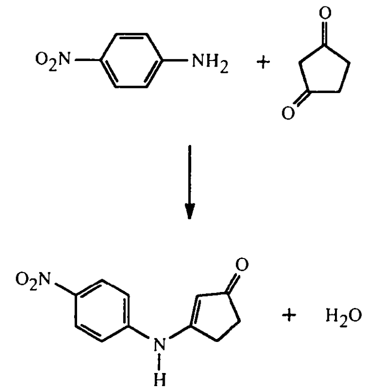
Abstract

The title compound, $C_{11}H_{10}N_2O_3$, is composed of a nitroanilino moiety and a cyclic α,β-unsaturated ketone moiety. The cyclic α,β-unsaturated ketone moiety forms a planar conformation, whereas the nitro group in the nitroanilino moiety is slightly out from the phenyl ring least-squares plane. The least-squares planes of the phenyl ring and the α,β-unsaturated ketone group are almost coplanar with respect to one another. The shortened C7—N1 and C8—C9 bond lengths suggest that the amino group is conjugated with the α,β-unsaturated ketone group. Intermolecular hydrogen bonds between the carbonyl O atom and the amino group link the molecules into infinite chains [N—H 0.87 (2), $\text{H}\cdots\text{O}^{\text{i}}$ 1.95 (2), $\text{N}\cdots\text{O}^{\text{i}}$ 2.812 (4) Å and $\text{N—H}\cdots\text{O}^{\text{i}}$ 169 (2)°; symmetry code: (i) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$].

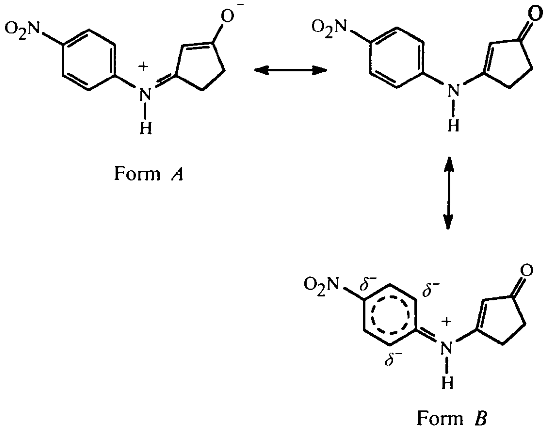
Comment

Nitroanilines and nitroaniline derivatives have long been of interest in non-linear optical (NLO) materials because of their inherently large molecular polarizability (β) (Williams, 1984). Hydrogen-bonding interactions have been found to be important in the non-centrosymmetric crystal packing of nitroanilines (Panunto, Urbanczyk-Lipkowska, Johnson & Etter, 1987) and other organic compounds (Zyss, Nicoud & Coquillay, 1984). In our continuing research on designing NLO materials using hydrogen-bonding interactions (Etter & Frankenbach, 1989; Etter & Huang, 1992), the title compound, (I), was synthesized from the reaction of *p*-nitroaniline with 1,3-cyclopentanedione.



(I)

X-ray analysis shows that the title compound is composed of a nitroanilino moiety and a cyclic α,β-unsaturated ketone moiety. The cyclic ketone moiety forms a planar conformation. The nitro group of the nitroanilino moiety is at an angle of 9.8 (4)° to the phenyl ring least-squares planes. The least-squares planes of the phenyl ring and the α,β-unsaturated ketone group are almost coplanar with respect to one another, with a dihedral angle of 3.2 (4)° between them. The C7—N1 bond distance of 1.358 (2) Å is slightly shorter than that of C1—N1 [1.389 (2) Å], suggesting that the lone pair of electrons in the amino group is more likely delocalized into the cyclic α,β-unsaturated ketone group than into the nitrophenyl group; thus, the resonance form *A* is more favorable than the resonance form *B*, shown below.



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