

# The Crystal and Molecular Structure of 2,2'-Diaminodiphenyl at $-165\text{ }^{\circ}\text{C}$

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The structure of the title compound has been determined by X-ray crystallographic methods using 2406 observed reflections collected by counter methods at  $-165\text{ }^{\circ}\text{C}$ . The compound crystallizes in the space group  $C2/c$  with four molecules per unit cell with a crystallographically determined twofold axis through the central carbon-carbon bond of the molecules. The structure model was refined to a conventional  $R$  of 0.045. In order to remove the influence of the asphericity of the valence electron densities all reflections with  $\sin \theta/\lambda < 0.65\text{ \AA}^{-1}$  were excluded from the final refinements of the nonhydrogen atoms leaving 1353  $F_{\text{obs}}$ 's ( $R = 0.034$ ,  $R_w = 0.040$ ). The angle between the planes of the phenyl rings is  $58.2^{\circ}$  with the amino groups *syn*. The determining factor in the configuration is probably the *intra*-molecular  $\text{N}\cdots\text{N}$  hydrogen bond with  $\text{N}\cdots\text{N}$  distance  $2.933(1)\text{ \AA}$ . The hydrogen arrangement in the amino groups is disordered such that each nitrogen is either donor in an *intra*-molecular hydrogen bond and acceptor in an *inter*-molecular hydrogen bond or *vice versa*. The bond lengths and bond angles in the phenyl rings indicate significant deformations of the ring.

Structure investigations of 2,2'-disubstituted biphenyls in the gas<sup>1-3</sup> and crystalline<sup>3-6</sup> states have shown the preferred conformation to be *syn*, with the rotation angle between the ring planes ( $\phi$ ) varying from  $60^{\circ}$  in 2,2'-difluorobiphenyl<sup>1</sup> to  $86^{\circ}$  in 4,4'-diamino-2,2'-dimethylbiphenyl<sup>6</sup> ( $\phi = 0$  for *syn*-periplanar). The value of  $\phi$  found for 2,2'-dichlorobiphenyl<sup>3</sup> is about  $70^{\circ}$  both in the crystalline and gaseous state and a similar value ( $\phi = 72^{\circ}$ ) was obtained for 4,4'-diamino-2,2'-dichlorobiphenyl.<sup>5</sup> This value of  $\phi$  gives a relatively short *intra*-molecular  $\text{Cl}-\text{Cl}'$  distance of about  $3.42\text{ \AA}$  which leads to small deformations in the molecule,<sup>3</sup> an opening of the  $\text{Cl}'-\text{Cl}-\text{C}2$  angles to  $123.0^{\circ}$

and the  $\text{C}2-\text{Cl}$  bond is bent  $2.3^{\circ}$  out of the plane of the phenyl ring. The energies involved in these deformations are probably small, similar deformations were also found in the crystal structure investigations of 3,3'-dimethyl-<sup>7</sup> and 3,3'-dichloro-4,4'-diaminobiphenyl.<sup>8</sup>

The preferred *syn* conformation of the 2,2'-disubstituted biphenyls imply that van der Waals type interactions between the substituents must play a dominant part in the conformational structure of biphenyls. In support of this are the *trans* conformations found in the crystal structure investigations of the two 3,3'-disubstituted biphenyls.<sup>7,8</sup> In these cases the deciding factors must be the conjugation over the  $\text{C}1-\text{C}1'$  bond, interactions between the hydrogens at the 2, 2', 6 and 6' positions and packing effects. The rotation barrier in biphenyl is small, *ab initio* calculations<sup>9</sup> indicated a minimum of  $\phi = 32^{\circ}$ ,  $1.2\text{ kcal/mol}$  lower than for  $\phi = 0$  and  $4.5\text{ kcal/mol}$  lower than for  $\phi = 90^{\circ}$ . A  $\phi$  of about  $42^{\circ}$  was obtained in the electron diffraction studies of gaseous biphenyl<sup>10,11</sup> whereas a planar structure was found in the crystal structure investigation.<sup>12</sup>

In order to gain more information on the conformations of biphenyls a crystal structure investigation of 2,2'-diaminobiphenyl was carried out. The factor controlling the conformation in this case should be the probable formation of an *intra*-molecular  $\text{N}\cdots\text{N}$  hydrogen bond.

## EXPERIMENTAL

An approximately cube-shaped crystal with edges of about  $0.4\text{ mm}$  was mounted on a computer-controlled Syntex PI four-circle dif-

fractometer with scintillation detector and equipped with incident-beam graphite monochromatized MoK $\alpha$ -radiation and a modified Enraf-Nonius low-temperature device (liquid N<sub>2</sub>). The temperature at crystal site was -165 °C. The axial solutions from the angular coordinates of fifteen reflections implied a monoclinic system. The systematic absences found in a fast low-angle datacollection were those of space group *Cc* or *C2/c*, and the cell volume indicated four molecules in the unit cell. The later structure determination showed the space group to be *C2/c*. Unit cell dimensions were determined by a least-squares treatment of fifteen reflections with  $2\theta$ -values between 40 and 45°.

Three-dimensional intensity data were recorded using the  $\omega$ - $2\theta$  scanning mode with scan speed variable from 3 to 12° min<sup>-1</sup> depending on the intensity of the reflection as determined by the counts in a 2 s scan over the reflection. Scan area was from [ $2\theta(\alpha_1) - 0.8^\circ$ ] to [ $2\theta(\alpha_2) + 1.1^\circ$ ] and background counting time was equal to 0.7  $\times$  scan time. Reflections with  $2\theta$ -values larger than 45° which had integrated counts of less than 10 cps determined in the 2 s scan were not recorded. The variations in the intensities of three standard reflections which were remeasured after every 60 reflections were random and accordingly no corrections were applied to the intensity data for these variations.

The estimated standard deviations were taken as the square root of the total counts with a 2 % addition of the net intensity for experimental uncertainties. Of the 2729 symmetry-independent reflections recorded ( $2\theta_{\max} = 90^\circ$ ), 2406 had intensities larger than twice their standard deviations. These were regarded as "observed" reflections and the remaining were excluded from the refinements. The intensities were corrected for Lorentz and polarization effects. The computer program used, as well as programs subsequently employed, is part of a local assembly of computer programs for CYBER-74 which is described in Ref. 13.

The atomic scattering factors used were those calculated by Doyle and Turner<sup>14</sup> for nitrogen and carbon and of Stewart *et al.*<sup>15</sup> for hydrogen.

#### CRYSTAL DATA

2,2'-Diaminobiphenyl, C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>, *M* = 184.21 amu, space group: *C2/c*, cell dimensions at -165 °C: *a* = 19.463(4) Å, *b* = 6.211(1) Å, *c* = 8.305(2) Å,  $\beta$  = 104.93°(2), *V* = 970.0(3) Å<sup>3</sup>, *Z* = 4, *D*<sub>calc</sub> = 1.261 g cm<sup>-3</sup>, *F* (000) = 392.

#### STRUCTURE DETERMINATION AND REFINEMENTS

The phase problem was solved by the MULTAN program assembly<sup>16</sup> in combination

with the use of negative quartets,<sup>17</sup> assuming the centrosymmetric space group *C2/c* which requires the molecule to possess a two-fold axis of symmetry.

The structure model was refined with isotropic temperature factors to a conventional *R* of 0.14. At this point anisotropic temperature factors were introduced for the nonhydrogen atoms. Least-squares refinements lowered *R* to 0.07 and *R*<sub>w</sub> to 0.12. The factor minimized was  $\sum w\Delta F^2$  with  $w = 1/\sigma(F_{\text{obs}})$ . A difference Fourier synthesis revealed the positions of the six hydrogen atoms. The four hydrogens bonded to the phenyl ring and one of the hydrogens of the amino-group showed up as the five highest peaks in the difference map (peak heights: 0.8–0.6 e Å<sup>-3</sup>), whereas the second hydrogen of the amino-group was distributed between two positions (peak heights: 0.4 e Å<sup>-3</sup>), one where it participated in an *intra*-molecular hydrogen bond and one where it participated in an *inter*-molecular hydrogen bond. The twofold symmetry requires this hydrogen to be equally distributed between the two positions. The hydrogens, five with weights of 1 and two with weights of 1/2, were included in the refinements. Final least-squares refinement of all positional parameters, anisotropic thermal parameters for nonhydrogen atoms and isotropic thermal parameters for hydrogen atoms converged to an *R* of 0.045 and an *R*<sub>w</sub> of 0.060.

In order to remove the influence of the asphericity of the valence electrons on the atomic parameters refinements were carried out with a  $\sin \theta/\lambda$  minimum cutoff of 0.65 Å<sup>-1</sup>, leaving 1353 *F*<sub>obs</sub>'s. Earlier structure determinations<sup>18,19</sup> have implied that the asphericity of the electron densities has no effect on carbon and nitrogen parameters when this cutoff is used. Least-squares refinement of all parameters involving nonhydrogen atoms converged to an *R* of 0.034, an *R*<sub>w</sub> of 0.040 and an *R*<sub>t</sub> for the total data set of 0.043. The exclusion of low-angle data in the refinement resulted in significant changes, in the order of 0.002–0.005 Å, in the bond lengths.

Final atomic parameters for nonhydrogen atoms are listed in Table 1 together with those obtained for the hydrogen atoms in the refinement using all data. A list of observed and calculated structure factors is available from the author upon request. Standard deviations

Table 1. Fractional atomic coordinates and thermal parameters with estimated standard deviations. The anisotropic temperature factor is given by:  $\exp \{-2\pi^2[U_{11}(a^*h)^2 + \dots + 2U_{23}(b^*c^*hd)]\}$ .

Atom	x	y	z	U11	U22	U33	U12	U13	U23
C1	.03879(3)	.20678(7)	.25503(5)	.0178(2)	.0115(2)	.0140(2)	-.0008(1)	-.0004(1)	.0005(1)
C2	.08444(3)	.37382(8)	.33432(6)	.0230(3)	.0154(2)	.0130(2)	-.0052(2)	.0016(1)	-.0001(1)
C3	.15707(4)	.36210(13)	.34192(8)	.0243(3)	.0317(3)	.0201(2)	-.0128(2)	.0069(2)	-.0055(2)
C4	.18470(4)	.18918(18)	.27228(11)	.0218(3)	.0433(4)	.0275(3)	-.0930(3)	.0092(2)	-.0101(3)
C5	.14027(4)	.02356(12)	.19450(8)	.0208(3)	.0287(3)	.0226(2)	.0009(2)	.0048(2)	-.0037(2)
C6	.06817(3)	.03328(8)	.18810(6)	.0190(2)	.0146(2)	.0178(2)	.0014(1)	.0009(1)	-.0004(1)
N7	.05719(4)	.54854(8)	.40452(6)	.0319(3)	.0161(2)	.0168(2)	-.0072(2)	.0066(2)	-.0049(1)
Atom	x	y	z	B	Atom	x	z	B	
H3	.1901(6)	.4846(19)	.4006(16)	3.2(2)	H4	.1845(20)	.2794(16)	3.5(2)	
H5	.1583(6)	-.1004(20)	.7444(15)	2.8(2)	H6	-.0841(17)	.1330(12)	1.8(2)	
H71	.0914(7)	.6457(21)	.4621(17)	3.7(3)	H72A	.5232(30)	.4530(23)	1.4(3)	
H72B	.0240(11)	.6097(34)	.3289(27)	2.3(4)					

in molecular parameters were calculated from the correlation matrix ignoring standard deviations in cell parameters.

## DISCUSSION

Bond lengths and bond angles are listed in Fig. 1 where the numbering of the atoms is indicated, and deviations from planarity are given in Table 2. A view of the molecule as seen along the C1-C1' bond is given in Fig. 2. Each phenyl ring is planar with the nitrogen atom in the ring plane, whereas in 2,2'-dichlorobiphenyl<sup>3</sup> the C2-Cl bond was bent 2.3° out of the ring plane. The angle between the ring planes is 58.2°. In addition to a rotation around the central C1-C1' bond the rings are bent relative to each other, as showed by the difference in the two torsional angles C2-C1-C1'-C2' [59.79°(8)] and C6-C1-C1'-C6 [56.17°(9)], and the configuration around C1 is slightly nonplanar with C1 0.013 Å out of the plane through C2, C6 and C1'. The two C1'-C1-C2 angles are opened to 122.15° which gives a nonlinear C4-C1-C1'-C4' arrangement as can be seen in Fig. 2, in agreement with the results found for 2,2'-dichlorobiphenyl.<sup>3</sup>

The factor determining the configuration of the 2,2'-diaminobiphenyl molecule must be the *intra*-molecular N...N hydrogen bond. The hydrogen arrangement around the aminogroups is disordered (see Figs. 1 and 2), such that each nitrogen atom is either donor in an *intra*-molecular hydrogen bond (N-H72B...N, N...N: 2.933(1) Å, ∠N-H...N: 143°) and acceptor in an *inter*-molecular hydrogen bond (N...H72A-N, in position: -x, 1-y, 1-z, N...N: 3.107(1) Å, ∠N...H-N: 170°) or

Table 2. Deviations, Dev., (Å × 10<sup>3</sup>) from a least-squares plane through the six atoms in the phenyl ring.

Atom	Dev.	Atom	Dev.	Atom	Dev.
C1	-6	C6	7	H5	-7
C2	0	N7	4	H6	9
C3	4	C1'	15	H71	81
C4	-2	H3	12	H72A	475
C5	-3	H4	2	H72B	-680

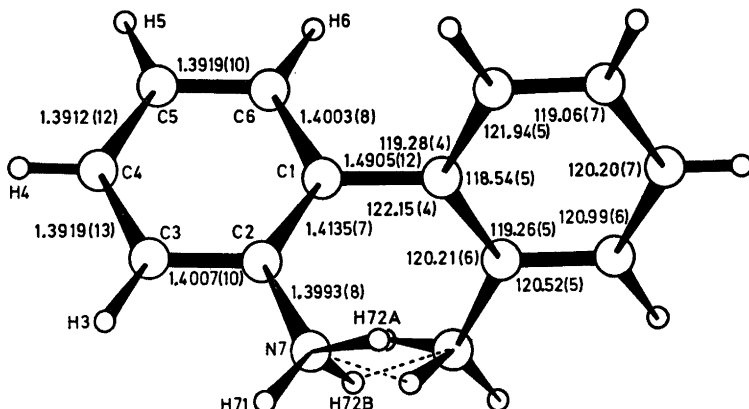


Fig. 1. Bond lengths (Å) and bond angles (°) with estimated standard deviations in the last digit of the corresponding number. The disordered *intra*-molecular hydrogen bond is indicated by broken lines. The results for the heavy atoms are based on the parameters obtained in the refinement using only high-angle data. The three C-N-H angles are: C2-N7-H71 114.8°; C2-N7-H72A 118.4°; C2-N7-H72B 109.3°.

*vice versa*. Each molecule has one *intra*-molecular hydrogen bond and participates in two *inter*-molecular hydrogen bonds, in one as a donor and in one as an acceptor.

The phenyl ring angles deviate significantly from 120°, the C2-C1-C6 angle is closed in agreement with results found for other biphenyls,<sup>3,7,8,12,20</sup> although the value found in the present case (118.54°) is significantly larger than those found in 2,2'-dichlorobiphenyl<sup>3</sup> (116.2°) and in biphenyl<sup>20</sup> (117.4°, corrected for thermal vibration effects). The relatively small angles found in other biphenyls may in part be due to both thermal vibration effects and the shifts of the atomic positions towards the center of the phenyl ring caused by the asphericity of the electron density. The closing of the C2-C1-C6 angle is probably caused by the conjugation over the C1-C1' bond (double bond character: 0.15). Similarly the closing of the C1-C2-C3 angle must be caused by the participation of the amino group in the conjugated system. Studies of acetamide and related systems<sup>21</sup> have shown that the O-C-C angle decreases with decreasing double bond character of the C-O bond and increasing double bond character of the C-N bond. The C2-N7 bond in the present case is short with a double bond character of 0.33 assuming N7 to be *sp*<sup>2</sup>-

hybridized, and the C1-C2 bond [1.4135(7) Å] is significantly longer than the standard benzene bond length of 1.396 Å. The conjugation over N7-C2-C1-C1'-C2'-N7' is probably enhanced by the hydrogen bonding.<sup>21</sup> The closing of the C6-C1-C2 and C1-C2-C3 angles and the lengthening of (*i.e.* decreased

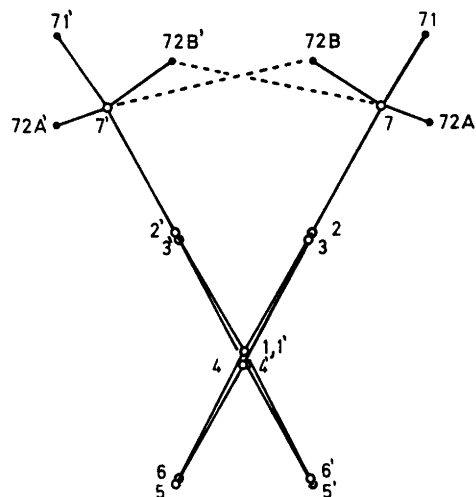


Fig. 2. 2,2'-Diaminobiphenyl as seen along the central carbon-carbon bond. The disordered *intra*-molecular hydrogen bond is indicated by broken lines.

conjugation over) the C1–C2 bond lead to the other deformations in the phenyl ring (see Fig. 1).

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