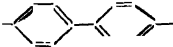


## Theoretical calculation of the crystal structure of benzidine

N A AHMED

Physics Department, National Research Centre, Dokki, Cairo, U.A.R.

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Benzidine  $\text{NH}_2$    $\text{NH}_2$  crystallises in the mono-

clinic system with a unit cell of dimensions  $a = 5.55 \text{ \AA}$ ,  $b = 7.644 \text{ \AA}$ ,  $c = 24.213 \text{ \AA}$ ,  $\beta = 102^\circ$ . There are four molecules in the unit cell related by the space group  $P2_1/c$ . Using the method of atom-atom potentials the lattice energy was calculated and two positions of the molecule were found to have minimum potential energy. The question about the coplanarity of the molecule could not be answered.

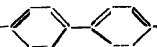
### 1. INTRODUCTION

The method of atom-atom potentials was used successfully in solving the crystal structure of some organic compounds. The structure having the minimum potential energy was found to agree well with the experimental structure determined by X-ray diffraction e.g.

- (1) the structure of tetraphenyltin (Ahmed, Kitaigorodsky & Mirskaya (1971))
- (2) the structure of 3,6-diphenyl-*s*-tetrazine (Ahmed & Kitaigorodsky 1972).
- (3) the structure of *p*-diethynylbenzene (Ahmed, Kitaigorodsky & Srota 1972)

The crystal structure of benzidine was not investigated before. Other benzidine complexes were studied by X-ray diffraction. The benzidine molecule was found not to be planar, but twisted around the C-C bond connecting the benzene rings. The dihedral angle was found to be  $19.6^\circ$  in benzidine-5-trinitro complex (Tachikawa, Yakushi & Kuroda 1974 and  $30.8^\circ$  in the complex between N,N,N',N'-tetramethyl benzidine and chloroami (Yakushi, Ikeneto & Kuroda 1971).

### 2. EXPERIMENTAL

Crystals of benzidine  $\text{H}_2\text{N}$ -- $\text{NH}_2$  were obtained by the

slow evaporation of its solution in ethyl alcohol and the crystals obtained are yellow thin plates. Rotation and Weissenberg photographs were taken using  $\text{CuK}$  radiation for the crystal mounted on the  $z$ -axis from which it was found that the molecules of benzidine crystallizes in the monoclinic form with the following unit cell dimensions  $a = 5.55 \text{ \AA}$ ,  $b = 7.644 \text{ \AA}$ ,  $c = 24.213 \text{ \AA}$ ,  $\beta = 102^\circ$ .

From the systematic absences (*h*0*l* with *l* odd *oko* with *k* odd) the space group was identified as  $P_{21}/c$ . With four molecules in the unit cell the calculated density is 1.21 gm/cm<sup>3</sup>.

### 3. CALCULATION OF THE STRUCTURE

Having four equivalent positions, the space group  $P_{21}/c$  requires each molecule to occupy general position. The benzidine molecule being non-planar increases the number of variables to be determined to seven, three angles of rotation of the whole molecule about three orthogonal axes, three translations along these axes and the angle of twist between the two phenyl rings. To identify these variables three axes were chosen  $XYZ$  such that  $X$  and  $Y$  coincide with the  $x$  and  $y$  crystallographic axes and the molecule is placed with its plane in the  $X-Z$  plane with the direction  $C_1-C_4-N_1$  along the  $X$ -axis and the point bisecting the  $C_1-C_7$  bond at the origin, figure 1. The first six variables are measured from this initial position and the angle of twist between the two rings is denoted by  $\gamma$ . The three rotational variables  $\psi$ ,  $\theta$  and  $\phi$  are the angles of rotation about the  $X$ ,  $Y$  and  $Z$  axes, and the three translational variables  $TA$ ,  $TB$ ,  $TC$  are the projections of the distance between the point bisecting  $C_1-C_7$  and the origin on the three axes  $XYZ$ .

The molecule has to be rotated from  $\psi = 0^\circ$  to  $90^\circ$ , from  $\phi = 0^\circ$  to  $90^\circ$ , from  $\theta = 0^\circ$  to  $180^\circ$  and from  $\gamma = 0^\circ$  to  $40^\circ$ . For the translations  $TA$ ,  $TB$  and  $TC$  the limits are from the origin up to  $a/2$ ,  $b/2$  and  $c/2$ .

The lattice energy was calculated at intervals of  $10^\circ$  for the angles of rotation and at intervals of  $0.4 \text{ \AA}$  for the translations. The function used is the Buckingham potential functions  $E = -A/r^6 + B e^{-ar}$ .

Summation was carried over all intermolecular distances within a sphere of  $10 \text{ \AA}$ . The  $A$ ,  $B$  and  $\alpha$  used are those of Kitaigorodsky (1966) for the interactions  $C \dots C$ ,  $C \dots H$  and  $H \dots H$ , table 1. For nitrogen interactions, the potential curves determined by Mirskaya & Nauchitel (1972), were used. Those curves gave agreement in case of  $N_2O$ ,  $\alpha\text{-N}_2$  and 3,6-diphenyl-*s*-tetrazine. The dimensions used for the molecule are such that

C-C within the phenyl ring =  $1.39 \text{ \AA}$

C-C between the two phenyl rings =  $1.50 \text{ \AA}$

C-N =  $1.426 \text{ \AA}$

C-H =  $1.084 \text{ \AA}$

N-H =  $1.05 \text{ \AA}$

The angle  $H \dots N \dots H = 120^\circ$

Table 1 Interaction Curves

	$A$ (Kcal.mole <sup>-1</sup> )	$B$ (Kcal.mole <sup>-1</sup> × 10 <sup>4</sup> )	$\alpha \text{Å}^{-1}$
C . C	358.0	4.2	3.58
C . H	154.0	4.2	4.12
H . H	57.0	4.2	4.86
H . N	259.0	4.2	3.78
N . C	305.0	4.2	3.69
N . H	128.0	4.2	4.25

The calculation was performed on the ICL 1905 computer using a program written by the author. The computing time was so long (about 20 hours) so it was done on intervals.

The lattice energy was found to be resistive to some variables specially to the angle  $\phi$ , while it is less sensitive to others ( $\theta$  and  $TB$ ) and approximately insensitive to the angle of twist between the two rings ( $\gamma$ ). Two positions of lowest energies were located at the values:

	$\psi$	$\theta$	$\phi$	$TA$	$TB$	$TC$	$E$
1st minimum	30°	75°	0.0	0.4	0.0	6.6	-20.45
2nd minimum	32°	113°	0.0	0.0	0.4	0.6	22.86

The second position of the molecule has lower energy, and so is more probable to be the correct one. As the values of energy are affected very little by the variation of the angle between the two rings it could not be concluded if the molecule is coplanar or not.

Table 2(a, b) gives the coordinates of the molecule corresponding to the two positions of minima assuming  $\gamma = 0.0^\circ$ . Collection of the three dimensional X-ray diffraction data and measuring of the X-ray intensities are going on. Least squares refinements are intended to be done for the two sets of coordinates given in table 3 to have a complete solution of the structure.

Table 2a

Atom	$x/a$	$y/b$	$z/c$
$C_1$	0.135	0 0	0.303
$C_2$	0.023	-0.079	0.343
$C_3$	0.138	-0.079	0.399
$C_4$	0.367	0.0	0.416
$C_5$	0.480	0.070	0.377
$C_6$	0.364	0.079	0.320
$N_1$	0.486	0.0	0.475
$C_7$	0.004	0 0	0.242
$C_8$	0.121	0.070	0.201
$C_9$	0.009	0.079	0.146
$C_{10}$	-0.223	0 0	0.129
$C_{11}$	0.336	-0.079	0.168
$C_{12}$	-0.220	-0.079	0.225
$N_2$	-0.342	0 0	0.071

Table 2b

	$x/a$	$y/b$	
$C_1$	-0.026	0.052	0.277
$C_2$	0.235	0.026	0.287
$C_3$	0.284	0.026	0.341
$C_4$	-0.124	0.052	0.385
$C_5$	0.085	0.131	0.375
$C_6$	0.134	0.131	0.321
$N_1$	-0.174	0.052	0.440
$C_1$	0.026	0.052	0.219
$C_2$	0.235	0.131	0.205
$C_3$	0.284	0.131	0.154
$C_4$	0.124	0.052	0.111
$C_5$	0.085	0.026	0.121
$C_6$	0.134	0.026	0.175
		0.052	

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