Experimental and Theoretical Determination of the Crystal Structure
of 3,6-Diphenyl-*s*-tetrazine

By N. A. Ahmed* and A. I. Kitaigorodsky

*Institute of Elemento-Organic Compounds, Academy of Sciences of the USSR,
Vavilova St. 28, V-312, Moscow, USSR*

3,6-Diphenyl-*s*-tetrazine forms monoclinic crystals with $a = 5\cdot415$, $b = 5\cdot183$, $c = 20\cdot603$ Å, $\beta = 101°30'$. There are two molecules in the unit cell in the space group $P2_1/c$. The structure was determined experimentally by X-ray three-dimensional analysis. The molecule is centrosymmetrical and planar. Theoretical calculation of the packing position of the molecule was carried out using the atom–atom potentials method. The orientation of the molecule in the unit cell is in agreement with that determined experimentally. The molecule is exactly or approximately planar.

Introduction

The method of atom–atom potentials was previously used by us to determine the structure corresponding to minimum potential energy. In the case of tetraphenyltin, good agreement was obtained with the X-ray diffraction analysis of Ahmed, Kitaigorodsky & Mirskaya (1971).

The structure of 3,6-diphenyl-*s*-tetrazine

$$H_5C_6-C\underset{N-N}{\overset{N=N}{\diagdown\diagup}}C-C_6H_5$$
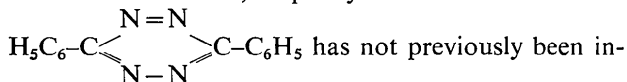
has not previously been investigated. It was thus interesting to determine whether such a molecule is completely planar, as in the case of *p*-terphenyl, or not.

Experimental

Samples of 3,6-diphenyl-*s*-tetrazine were supplied by Prof. J. Postovsky. Crystallization from ethanol gave pink monoclinic needles with the *b* axis as the needle axis. The three-dimensional X-ray data (taken with Cu $K\alpha$ radiation), were collected from equi-inclination Weissenberg photographs of a crystal rotating around the *a* and *b* axes. The unit-cell dimensions as measured from copper-calibrated zero-layer Weissenberg photographs are: $a = 5\cdot415 \pm 0\cdot004$, $b = 5\cdot183 \pm 0\cdot004$, $c = 20\cdot603 \pm 0\cdot009$ Å, $\beta = 101°30' \pm 6'$. The measured density of $1\cdot35$ gm.cm^{-3} agrees well with the value of $1\cdot30$ gm.cm^{-3} calculated for a two-molecule unit cell. The diffraction symmetry $2/m$ and systematic absences $0k0$ with k odd and $h0l$ with l odd suggested the space group $P2_1/c$.

The relative intensities were measured visually by using the multiple film technique (four films) and an intensity scale. 650 independent reflexions were recorded. The data were corrected for the Lorentz and

polarization effects. No absorption correction was applied. Inter-layer scale factors connecting the layers perpendicular to the *b*-axis were obtained using the other set of layers perpendicular to the *a*-axis. These scale factors were used in the determination of the structure and in the preliminary refinements.

Structure determination

The space group $P2_1/c$ has four equivalent positions, while the number of molecules per unit cell is two. This implies that the centres of symmetry of the molecules must lie on the centres of symmetry of the unit cell, *i.e.* at 0,0,0 and $0,\frac{1}{2},\frac{1}{2}$. The structure of *s*-tetrazine

$$H-C\underset{N-N}{\overset{N=N}{\diagdown\diagup}}C-H$$
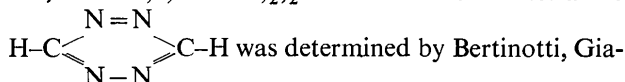
was determined by Bertinotti, Giacomello & Liquori (1956), and the molecule was found to be a planar one. In spite of these restrictions the possibility that the molecule of 3,6-diphenyl-*s*-tetrazine is not planar still exists. However it was assumed as a preliminary structure that the molecule is planar. The orientation of the plane of the molecule was determined from the three-dimensional Patterson maps. The atomic coordinates were then calculated assuming the dimensions of the molecules to be as follows: C–N = $1\cdot334$ Å, N–N = $1\cdot321$ Å, C–N–N = $115°57'$, N–C–N = $127°22'$, (Bertinotti *et al.*, 1956), C–C distance between rings = $1\cdot48$Å. These coordinates gave a reliability factor $R = \sum||F_o| - |F_c||/|F_o|$ of $0\cdot30$. A refinement process was then begun with three dimensional Fourier summations. After two successive electron density calculations, there were no shifts in the coordinates and the reliability factor was $0\cdot24$. The coordinates, individual isotropic temperature factors and inter-layer scale factors were then refined in a series of least-squares calculations. The refinement was based on minimizing the function $\sum w(|F_o| - |F_c|)^2$. The weights were calculated according to the equation, $w = 1/a + |F_o| + c|F|^2$, where $a = 2\cdot0 \times |F_{min}|$ and $c = 2/|F_{max}|$. After three cycles the

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* Permanent address: Department of Physics, National Research Centre, Dokki, Cairo, A.R.E.

reliability factor was reduced to 0·130. The final atomic coordinates are given in Table 1. The atomic scattering factors used were those of Hanson, Herman, Lea & Skillman (1964). Fig. 1 shows the bond lengths and valency angles of the molecule. Fig. 2 shows the short intermolecular distances. The molecule is planar with an angle between the central ring and the phenyl ring of one degree. The maximum deviation from the best plane passing through the whole molecule and the origin of the unit cell is 0·025 Å.

Table 1. Experimental coordinates

	x/a	y/b	z/c	B
N(1)	−0·1224	0·0271	0·0502	3·073
N(2)	0·1964	0·1531	−0·0057	3·301
C(1)	0·0743	0·1800	0·0443	2·801
C(2)	0·1603	0·3752	0·0944	2·835
C(3)	0·0299	0·4094	0·1470	3·559
C(4)	0·1078	0·6008	0·1936	3·603
C(5)	0·3131	0·7675	0·1897	3·690
C(6)	0·4402	0·7358	0·1373	4·170
C(7)	0·3630	0·5400	0·0895	3·628

Theoretical calculation

As the molecule of 3,6-diphenyl-s-tetrazine contains nitrogen atoms, the interactions of which with neighbouring hydrogen atoms are not known to a high degree of accuracy, it was thought that calculation of the conformation of the molecule would not be accurate. The angle between the central ring and the phenyl groups, which is the only degree of freedom in the molecular structure was included in calculating the intermolecular energy. For nitrogen intermolecular interactions the potential curves, Table 2, determined recently by Mirskaya & Nautchitel (1972), can be safely used. The above authors tested the curve for the crystals of N_2O and α-N_2 and found a good agreement between the calculated lattice energies and the experimental values of heat of sublimation. Agreement was also found between the calculated and experimental lattice parameters. Kitaigorodsky's (1966) parameters for C···C, C···H and H···H, were used for such interactions. The lattice energy was obtained by the evaluation of the Buckingham potential function: $E = -Ad^{-6} + B\exp(-\alpha d)$.

Table 2. Interaction curves for nitrogen (1)

	A kcal/mole Å^6	B kcal/mole	αÅ^{-1}
N···N	259	4·2 × 10^4	3·78
N···C	305	4·2 × 10^4	3·69
N···H	128	4·2 × 10^4	4·25

As the translational degrees of freedom were deleted, the problem was reduced to one of four degrees of freedom, namely the rotational variables of the whole molecule θ, φ, ψ and the angle γ between the central and the phenyl ring. The angles θ, φ, ψ are defined as follows. We assume a cartesian reference system $X\,Y\,Z$

with X and Y coincident with the x and y crystallographic axes. Starting with the axis of the molecule $C(1)\cdots C(2)\cdots C(5)$ coincident with the X axis and the phenyl rings lying in the XZ plane, the final position of the molecule is reached by a rotation θ around X, followed by a rotation φ around Z and a rotation ψ around Y. The range of θ was from −90 to +90°, of φ from 0 to 90°, of ψ from 0 to 180° and of γ from −30 to +30°. In the first set of calculations the scanning interval for the four angles was 10°. Two regions of lowest energy were found. A second set of calculations were then carried on for these regions with a scan of 5°. One minimum was found to be lower than the other. Fig. 3 shows the iso-energetic curves at the nearest regions to that minimum. The map giving the variation of energy with θ and γ does not show a good minimum and the value of γ could not be determined accurately. The difference between the energies at $\gamma = 0°$ and $\gamma = 5°$ is only 0·1 kcal/mole. The values of θ, φ and ψ derived from these curves are $\theta = 22$, $\varphi = 45$, $\psi = 78°$. The corresponding values derived from the experimental results are $\theta = 22$, $\varphi = 45$, $\psi = 76°$. Table 4 gives the theoretical coordinates with the value of $\gamma = -6°$. The negative sign means that the rotation is in the reverse direction of θ. It is quite understandable that the difference between the experimental and theoretical coordinates which is more distinct in the coordinates of the short axes a and b is due not only to the difference in the orientation of the molecule but also to the difference in its dimensions.

Table 3. Interaction curves for nitrogen (2)

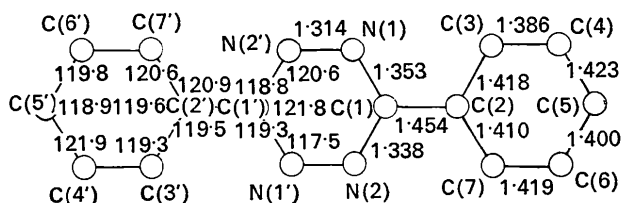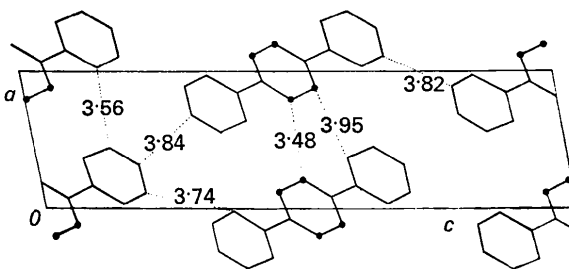|	A kcal/mole Å^6	B kcal/mole	αÅ^{-1}
N···N	187	4·2 × 10^4	3·99
N···C	261	4·2 × 10^4	3·77
N···H	107	4·2 × 10^4	4·38

Fig. 1. Molecular dimensions of 3,6-diphenyl-s-tetrazine.

Fig. 2. Intermolecular C–C and C–N distances obtained from experimental analysis.

Table 4. *Theoretical coordinates*

	x/a	y/b	z/c
N(1)	−0·146	0·045	0·046
N(2)	0·216	0·135	−0·001
C(1)	0·066	0·171	0·043
C(2)	0·145	0·372	0·094
C(3)	0·013	0·406	0·145
C(4)	0·089	0·595	0·192
C(5)	0·293	0·752	0·189
C(6)	0·425	0·718	0·138
C(7)	0·351	0·529	0·091

The effect of any variations in the potential curves of nitrogen (Table 2) on the above parameters was tested by using other curves (Table 3) calculated from the universal formula

$$E = -\frac{0·119 d_o^{\,6}}{d^6} + 4·2 \times 10^4 \exp[-(13·6 d/d_o)].$$

Here, d_o is the sum of the van der Waals radii of the interacting atoms increased by 10%. The value of van der Waals radius for nitrogen used is 1·55 Å (Bondi, 1964). The parameters obtained were exactly the same and only the value of the energy was increased by about 1·0 kcal/mole.

Similar calculation was carried out for the structure of *p*-terphenyl using the unit-cell dimensions given by Dejace (1966). The same angle of $\gamma = 6°$ was obtained, in spite of the experimental planar result. These differences between the theoretical and experimental results may be due to either of the following reasons:

(i) the inaccuracy of the method of atom–atom potentials.

(ii) the non-addition of the energy of the isolated molecule to the lattice energy: the energy of the molecule is the summation of four factors (Casalone, Mariani, Mugnoli & Simonetta, 1968), one of which is the π-electron interaction which tends to make the molecule planar.
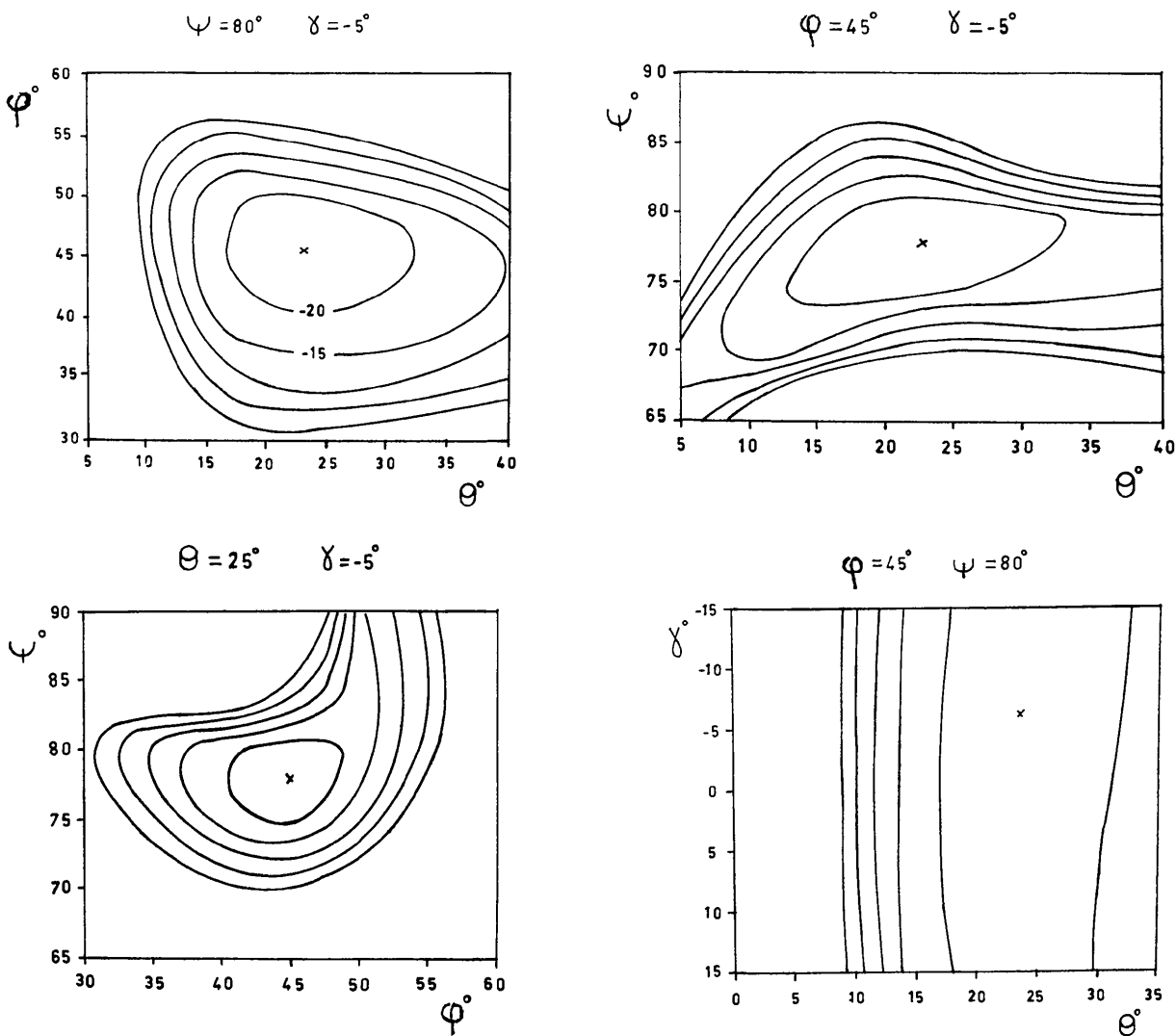

Fig. 3. Iso-energetic curves for crystal lattice.

However, one can conclude that the planarity of the molecule of 3,6-diphenyl-*s*-tetrazine or *p*-terphenyl is the result of the intermolecular interactions rather than the result of the π-electron energy of the isolated molecule.

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# The Crystal Structure of C₁₀H₁₄N₄O₂, a Heterocyclic Cage Compound

By RICHARD D. GILARDI

Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, D.C. 20390, U.S.A.

A heterocyclic cage ($C_{10}H_{14}N_4O_2$) was recently synthesized from ethylenediamine and glyoxal. Through crystal-structure analysis, the molecule was shown to be a rigid cage containing five-, six-, and seven-membered saturated heterocyclic rings. The compound crystallizes in space group $C2/c$ with $a = 11\cdot271 \pm 0\cdot007$, $b = 5\cdot983 \pm 0\cdot004$, $c = 14\cdot755 \pm 0\cdot009$ Å, and $\beta = 106\cdot1 \pm 0\cdot1°$. The asymmetric unit is a half-molecule ($Z = 4$), and the calculated crystal density is $1\cdot545$ g.cm^{-3}. X-ray intensity data were collected with an automatic diffractometer and refined to $R = 0\cdot053$. The structure was solved by the symbolic addition procedure for direct phase determination.

Introduction

A new reaction between ethylenediamine (I) and glyoxal (II) was recently reported by Edwards, Weiss, Gilardi & Karle (1968). A dilute aqueous solution of (I) and (II), in the molar ratio 2:3, reacted at room temperature to form a cage compound (III), $C_{10}H_{14}N_4O_2$. Several distinct structural formulae are compatible with the chemical properties, nuclear magnetic resonance spectrum, and mass spectrum of this substance. Two possibilities are shown below:
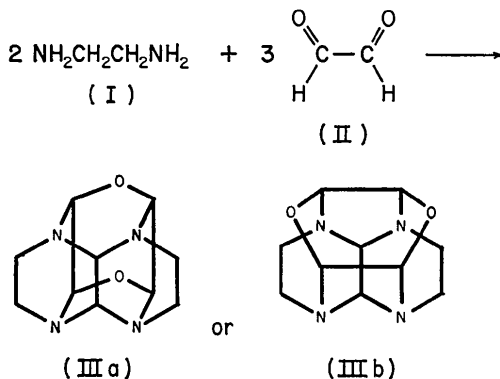
(IIIa)   (IIIb)

Structure (IIIa) is composed entirely of six-membered heterocyclic rings, while (IIIb) contains five-, six-, and

seven-membered rings. Nevertheless, the environment of bonded neighbors about any chosen atom of (IIIa) is identical to the bonded environment of a corresponding atom of (IIIb), e.g., the N atoms are adjacent to one secondary and two tertiary carbon atoms in (IIIa) or (IIIb). The analysis of the X-ray diffraction data from a crystal of this substance unambiguously indicated (IIIb) to be the correct structure. Crystals of this substance were obtained from Drs J. M. Edwards and U. Weiss of the National Institute for Arthritis and Metabolic Diseases.

Experimental

Crystals were grown from ethanol. The examination of the X-ray diffraction pattern of these apparently single crystals revealed that they were multiple. The material was extremely soluble in water, and it was found that single crystals could be quickly grown from a few drops of water on a microscope slide. The sharp diffraction pattern obtained from these crystals was identical in its spacings with the diffuse patterns obtained from the crystals grown from ethanol. A melting-point determination indicated no difference between the original and the recrystallized material.

Precession and Weissenberg diffraction photographs indicated that the crystal is monoclinic, with systematic absences characteristic of either of the space groups $C2/c$ or Cc. Cell dimensions were obtained by aligning