Crystal Structure of p-Diethynylbenzene

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Crystals of p-diethynylbenzene, $C_{10}H_6$, are monoclinic with $a=4\cdot007$, $b=6\cdot018$, $c=15\cdot340$ Å, $\beta=91°42'$. The space group is $P2_1/c$ with two centrosymmetric molecules in the unit cell. The structure was determined from three-dimensional Patterson maps with the aid of the calculation of molecular packing using the method of atom–atom potentials. The $C\equiv C$ bond length is $1\cdot188$ Å, with the carbon atoms lying approximately in the plane of the benzene ring. The experimental and theoretical structures are in good agreement.

Introduction

The potential curves of $C\cdots C$, $C\cdots H$ and $H\cdots H$ interactions given by Kitaigorodsky (1966) have been used to calculate the molecular packing in several compounds. They proved to give good agreement with the X-ray results for structures such as naphthalene and anthracene (Mirskaya & Kozlova, 1969), tetraphenyltin (Ahmed, Kitaigorodsky & Mirskaya, 1971) and 3,6-diphenyl-s-tetrazine (Ahmed & Kitaigorodsky, 1972). In these compounds the intramolecular bonds were either single or conjugated bonds in aromatic rings. In the present structure there is a carbon–carbon triple bond, and it is the aim of this work to test the validity of the above curves in such structures.

Experimental

Crystals of p-diethynylbenzene $HC\equiv C-\!\!\left\langle\bigcirc\right\rangle\!\!-C\equiv CH$ are volatile (m.p. 98°C). For X-ray work small crystals were enclosed in very thin glass capillary tubes. The crystal is monoclinic with dimensions $a=4\cdot007$; $b=6\cdot018$; $c=15\cdot340$ Å and $\beta=91°42'$. The space group $P2_1/c$ was assigned on the basis of the extinction of reflexions ($h0l$ with l odd and $0k0$ with k odd). The measured density of $1\cdot16$ g.cm^{-3} agrees well with value of $1\cdot13$ g.cm^{-3} calculated for a two-molecule unit cell. 274 independent reflexions were collected

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from equi-inclination Weissenberg photographs taken with the crystal rotating around the b axis. The relative intensities were measured visually using the multiple-film technique (four films). The layers were related by using two other layers taken with the crystal rotating around the c axis. The scale factors obtained were only used in calculating the Patterson function.

Structure determination

The structure was determined by making use of the Patterson maps together with the calculation of the packing position of the molecule using the method of atom–atom potentials. The space group requires the two molecules to have their centres of symmetry fixed at 0,0,0 and 0, $\frac{1}{2}$, $\frac{1}{2}$ and thus only the orientation of the molecule in the unit cell needs to be found. To identify the orientation, three rotational variables θ, φ, ψ were defined referred to a Cartesian system XYZ with X and Y coincident with the x and y crystallographic axes. Assuming that the chain $C\equiv C-H$ is lying along the line $C(2')-C(2)$, we began with this direction coinciding with the X axis and with the plane of the benzene ring in the XZ plane. The molecule was then rotated by an angle θ around X, followed by a rotation φ around Z and a rotation of ψ around Y. The range of θ was $-90° \rightarrow +90°$, of φ $0 \rightarrow 90°$ and of ψ $0 \rightarrow 180°$. The lattice energy was then calculated every 5° for each angle using the function $U= -A/r^6 + Be^{-ar}$. The values of A, B and α used are those given by Kitaigorodsky (1966). No variations of the lattice

Table 1. *Experimental coordinates*

Values are $\times 10^4$.

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{13}
C(1)	−24	−617	869	760	292	34	2	26	1
C(2)	1275	1433	651	488	280	35	154	−6	1
C(3)	1303	2079	−236	711	297	39	−50	14	23
C(4)	2664	2914	1308	790	228	45	79	−15	−36
C(5)	3785	4169	1838	1133	328	50	−219	−15	−59
H(1)	−157	−1347	1493	49450					
H(2)	2536	3471	−439	12447					
H(3)	4602	5367	2069	34938					

constants were considered and the dimensions of the molecule were as follows: the C–C bond length within the phenyl ring is 1·39 Å; the C–C single bond is 1·541 Å; the C≡C length is 1·206 Å and the C–H length in the phenyl ring is 1·084 Å, and in the chain, 1·09 Å. Four regions of minimum energy were found at the following values of variables.

No	$\theta(°)$	$\varphi(°)$	$\psi(°)$	U, kcal.mole^{-1}
1	56	43	63	−10·9
2	113	2	63	−9·6
3	70	0	60	−9·3
4	122	37	−60	−10·5

From the Patterson maps only the bond C≡C (1·2 Å approximately) can be recognized. The direction of this vector defines only the two angles φ and ψ. The values obtained for these variables coincide with the values given above for the position of minimum No. 1. The coordinates of the molecule were calculated in this orientation and the structure factors calculated with these coordinates gave a reliability index $R = 0·28$ $(R = \sum |F_o| - |F_c| / \sum |F_o|)$. That was adequate to start a refinement process with Fourier syntheses and least-squares calculations. At first, 3 cycles of refinement were carried out to refine the 15 positional parameters of the carbon atoms, individual isotropic temperature factors and inter-layer scale factors; the R index was 0·16. The positional parameters of the hydrogen atoms were then considered and refinement was continued with anisotropic temperature factors for the C atoms and isotropic for the H atoms. The number of parameters was 62. The R index dropped finally to 0·092. The final parameters are given in Table 1. Table 2 gives the theoretical coordinates.

Table 2. *Theoretical coordinates*

Values are × 10³.

	x/a	y/b	z/c
C(1)	−3	−41	89
C(2)	123	157	59
C(3)	126	200	−29
C(4)	260	332	125
C(5)	366	469	176
H(1)	−6	−76	158
H(2)	224	356	−53
H(3)	463	592	222

Table 3. *Deviations of the atoms from the best plane passing through the benzene ring and the origin*

Deviation (Å × 10⁻³)

C(1)	−35
C(2)	24
C(3)	7
C(4)	−24
C(5)	−127
H(1)	−32
H(2)	152
H(3)	−84

Fig. 1 shows the position of lowest minimum obtained theoretically. Fig. 2. shows the molecular dimensions obtained experimentally.
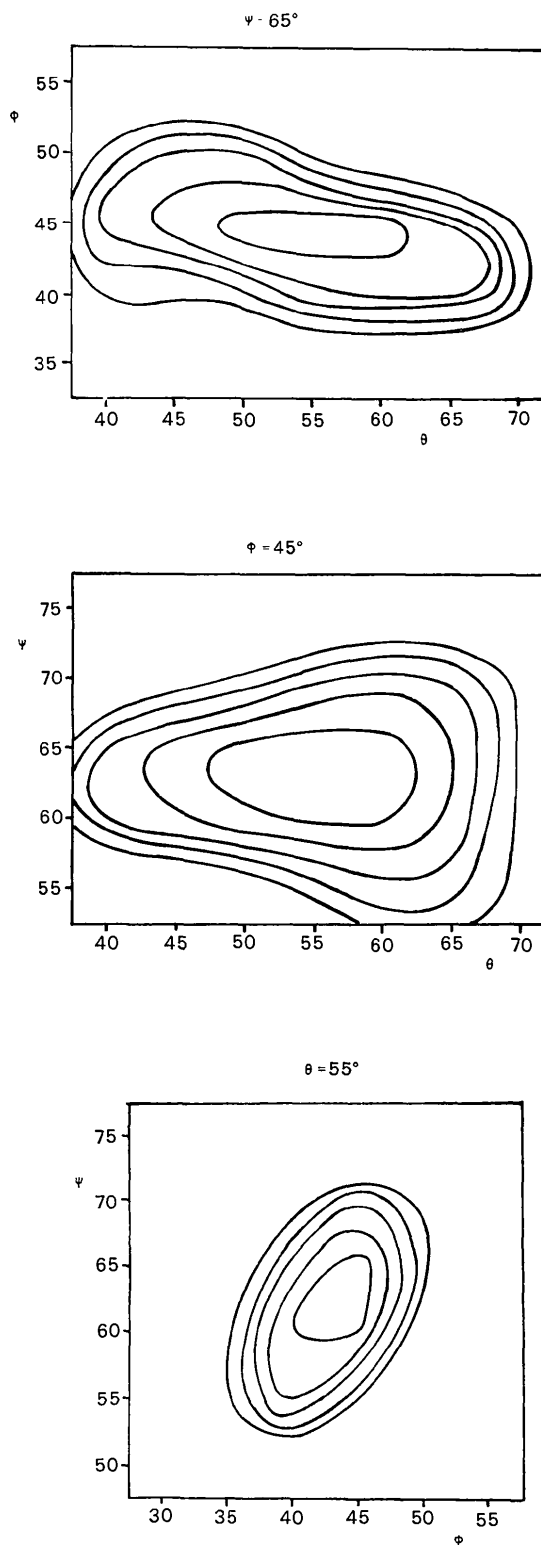

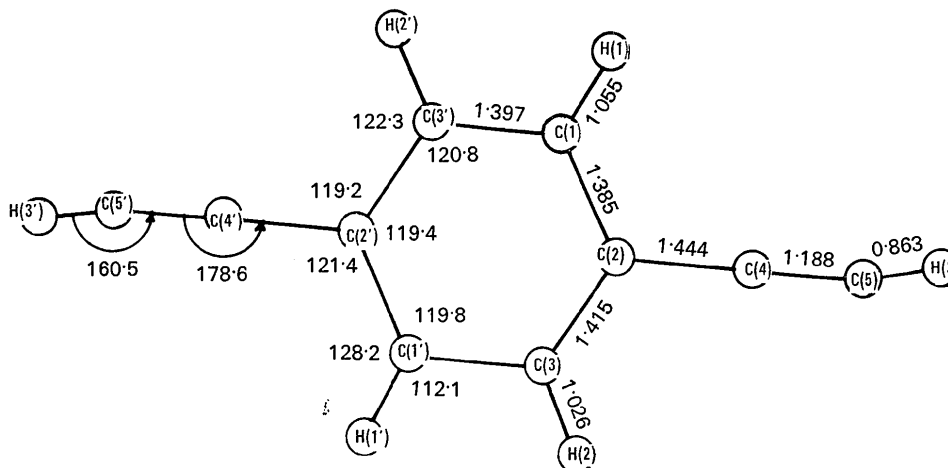Fig. 1. Theoretical position of lowest minimum.

Fig. 2. Experimental molecular dimensions.

Table 4. *Some intermolecular distances*

H···H	2·867 Å
H···H	3·034
H···H	3·059
H···H	3·254
H···H	3·299
C···H	2·949
C···H	3·561
C···H	3·863
C···C	3·641
C···C	3·714
C···C	3·718
C···C	3·796
C···C	3·856

The deviations of the atoms from the best plane passing through the benzene ring and the origin are given in Table 3. It is clear that C(4) and C(5) lie approximately in the plane of the benzene ring. The short intermolecular distances are given in Table 4.

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