THE CRYSTAL STRUCTURE OF *p*-AZO-TOLUENE (CH_3-$C_6H_4N)_2$

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KAPADIA[1] has studied the unit cell dimensions of *p*-azo-toluene. Its crystal structure has not been reported in literature so far. The present paper gives the complete structure by X-ray diffraction studies.

UNIT CELL AND SPACE-GROUP

p-azo-toluene crystallises in the form of thin narrow flat plates, the longer dimension being parallel to the *b*-axis. Rotation and Weissenberg photographs taken with the three crystallographic axes as axis of rotation gave the following cell data.

$a = 12{\cdot}01$ Å; $b = 5{\cdot}02$ Å; $c = 9{\cdot}32$ Å and $\beta = 90° 12'$.

The number of molecules per unit cell is 2. From the systematic absent reflections the space-group was confirmed to be $C_{2h}^5 - P\,2_1/a$.

INTENSITY MEASUREMENTS AND STRUCTURE DATA

The structure amplitudes were obtained from Weissenberg photographs (Cu-K_α radiation) using multiple film technique. The normal beam method was adopted for all photographs. The intensities were estimated visually by comparison with standard intensity spots. They were corrected for Lorentz, polarisation and temperature factors and later put on the absolute scale by the statistical method of Wilson. No absorption correction was made as the crystals used were very small.

DETERMINATION OF THE STRUCTURE

Since there are only two molecules per unit cell, each molecule must have a centre of symmetry. A Patterson projection using $(h\,0\,l)$ reflections was made, but it failed to give any clear indication of the benzene ring. Hence the method of 'trial and error' was adopted. As a first attempt the N–N bond of the two planar benzene rings was assumed to lie in the same plane as the rings. Because the molecule has a centre of symmetry such an assumption leads to the conclusion that the two rings must be coplanar. Structure factors were calculated with this structure. It was

noticed that no amount of adjustment could bring an agreement between the observed and the calculated structure factor values.

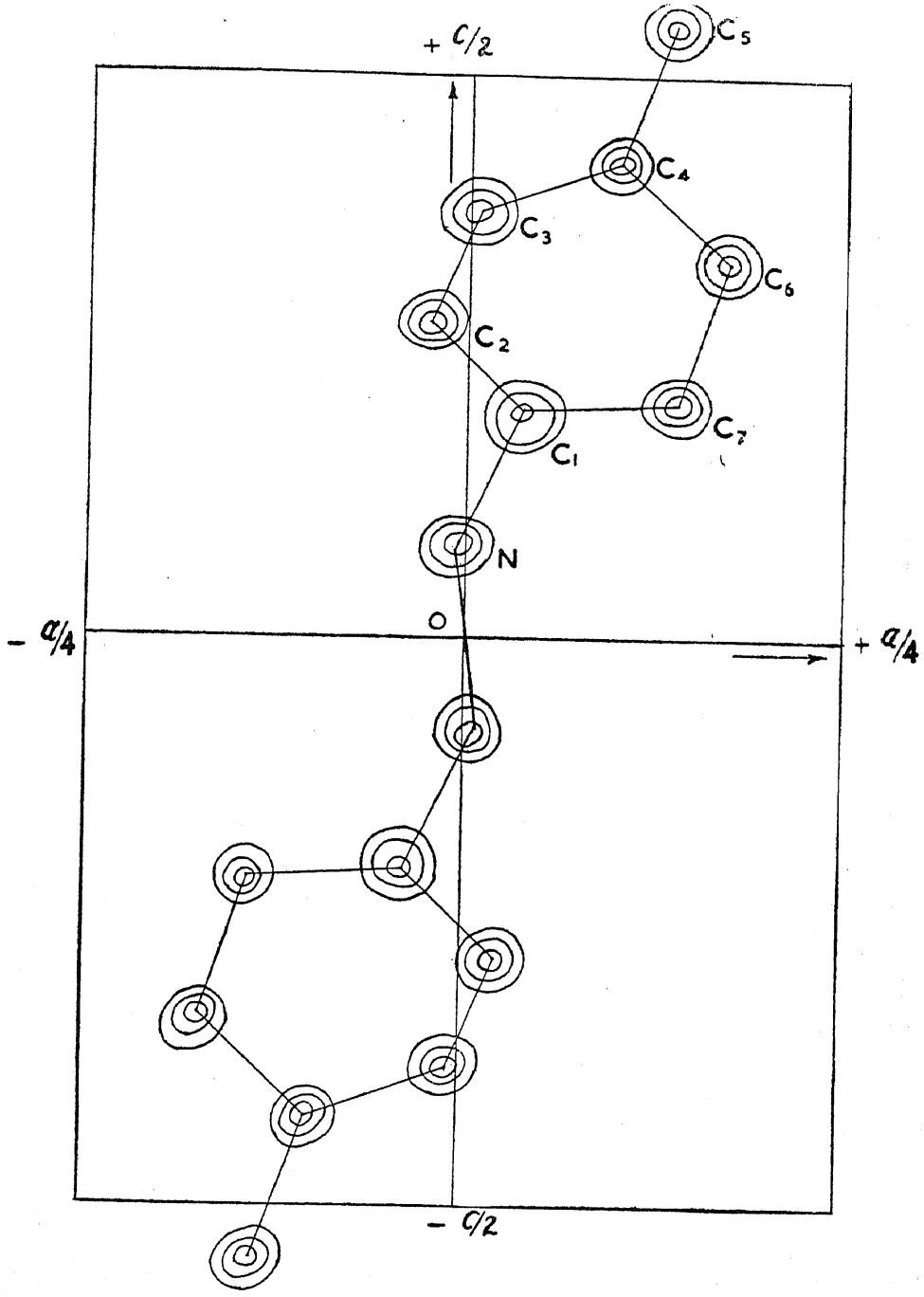

FIG. 1. Final electron density projection of *p*-azo-toluene on (*ac*) plane. Contours at arbitrary intervals.

A second series of trials was made with the two benzene rings attached by a central zig-zag bond, as in the case of dibenzyl. This gave structure

factors which were in fairly close agreement with the observed values. A number of refinements were then carried out with this model. Table I gives the atomic co-ordinates. The reliability factor for the $(h\,0\,l)$, $(h\,k\,0)$ and $(0\,k\,l)$ reflections with these co-ordinates was 0·17, 0·18 and 0·16 respectively.

TABLE I

Atom	Parameters		
	X	Y	Z
N	−0·010	0·035	0·069
C_1	0·044	0·208	0·203
C_2	−0·025	0·434	0·279
C_3	0·005	0·593	0·381
C_4	0·097	0·748	0·421
C_5	0·132	0·912	0·546
C_6	0·167	0·568	0·341
C_7	0·134	0·408	0·214

TABLE II

h k l	$F_{cal.}$	$F_{obs.}$	*h k l*	$F_{cal.}$	$F_{obs.}$	*h k l*	$F_{cal.}$	$F_{obs.}$
2 0 0	+60	48	6 0 3	+ 3	2	2 0 6	−36	29
4 0 0	+ 8	7	8 0 3	+ 3	2	4 0 6	−18	26
6 0 0	+40	36	2 0 4	+ 1	1	6 0 6	2	2
8 0 0	+21	17	4 0 4	+ 7	4	8 0 6	−29	25
2 0 1	−29	28	6 0 4	0	1	10 0 6	−30	28
4 0 1	+34	39	8 0 4	− 1	0	2 0 7	− 4	6
6 0 1	+ 9	10	10 0 4	− 3	2	6 0 7	−20	16
8 0 1	− 6	14	2 0 5	+ 7	6	8 0 7	−16	18
2 0 2	− 3	2	4 0 5	−18	16	8 0 8	+20	20
4 0 2	+ 3	4	6 0 5	−11	11	10 0 8	−19	17
6 0 2	+17	21	8 0 5	−15	13	2 0 9	+15	17
8 0 2	+ 7	10	10 0 5	+ 3	2	0 0 1	−36	32
2 0 3	+ 3	2	12 0 5	− 8	9	0 0 2	−26	30

TABLE II (*Contd.*)

h k l	$F_{cal.}$	$F_{obs.}$	h k l	$F_{cal.}$	$F_{obs.}$	h k l	$F_{cal.}$	$F_{obs.}$
0 0 3	− 4	8	4 0 $\bar{6}$	+ 5	12	2 3 0	+ 9	13
0 0 4	− 8	12	6 0 $\bar{6}$	+ 6	7	3 3 0	+16	9
0 0 7	−13	11	8 0 $\bar{6}$	+10	10	4 3 0	+ 3	2
0 0 9	+14	18	10 0 $\bar{6}$	− 2	2	5 3 0	+ 7	4
0 0 10	+15	21	2 0 $\bar{7}$	+ 2	1	6 3 0	+12	10
2 0 $\bar{1}$	+52	48	6 0 $\bar{7}$	− 6	4	1 4 0	+ 4	3
4 0 $\bar{1}$	+15	10	8 0 $\bar{7}$	+ 4	2	2 4 0	+11	7
6 0 $\bar{1}$	− 8	10	8 0 $\bar{8}$	−12	10	3 4 0	+ 6	5
8 0 $\bar{1}$	+ 8	10	10 0 $\bar{8}$	+ 1	0	4 4 0	+ 5	3
2 0 $\bar{2}$	−12	14	2 0 $\bar{9}$	−20	12	0 1 1	+13	8
4 0 $\bar{2}$	+13	14	0 2 0	+12	9	0 1 2	+28	40
6 0 $\bar{2}$	+ 4	3	0 4 0	+13	12	0 1 3	+35	30
8 0 $\bar{2}$	+11	12	1 1 0	+25	13	0 1 4	− 3	2
2 0 $\bar{3}$	−19	24	2 1 0	+22	26	0 1 5	+ 9	4
6 0 $\bar{3}$	+13	10	3 1 0	+ 5	7	0 1 6	− 8	3
8 0 $\bar{3}$	−17	15	4 1 0	− 5	8	0 1 7	+ 7	13
2 0 $\bar{4}$	−17	14	5 1 0	−10	15	0 1 8	−10	11
4 0 $\bar{4}$	−37	39	6 1 0	−11	9	0 1 9	+ 6	10
6 0 $\bar{4}$	−16	16	7 1 0	− 5	7	0 2 1	+ 3	2
8 0 $\bar{4}$	− 5	8	8 1 0	− 4	2	0 2 3	−13	24
10 0 $\bar{4}$	−23	20	9 1 0	+11	8	0 2 4	−16	26
2 0 $\bar{5}$	−17	19	1 2 0	+ 6	3	0 2 5	+17	22
4 0 $\bar{5}$	− 5	3	2 2 0	+ 4	2	0 2 6	+19	12
6 0 $\bar{5}$	−15	9	3 2 0	+11	8	0 2 6	+ 8	10
8 0 $\bar{5}$	−23	24	4 2 0	− 5	13	0 3 1	+10	18
10 0 $\bar{5}$	−13	16	5 2 0	−13	18	0 4 1	+13	10
12 0 $\bar{5}$	− 5	3	6 2 0	+18	12			
2 0 $\bar{6}$	− 8	8	1 3 0	+12	15			

In Table II the calculated and observed structure factor values are listed. Considering that the effect of hydrogen atoms was not taken into account, the agreement between the observed and calculated values is satisfactory.

Discussion of Structure

The bond-lengths and bond-angles are given below:—

C_1–C_2	1·42 Å	N–N–C_1	134° 30′
C_2–C_3	1·41	C_1–C_2–C_3	121° 15′
C_3–C_4	1·39	C_2–C_3–C_4	122° 20′
C_4–C_5	1·47	C_3–C_4–C_5	115° 20′
C_4–C_6	1·39	C_5–C_4–C_6	119° 28′
C_6–C_7	1·41	C_4–C_6–C_7	121° 14′
C_1–C_7	1·40	C_6–C_7–C_1	122° 5′
C_1–N	1·49	C_7–C_1–C_2	121° 30′
N–N	1·27	(error in bond angles ± 2°)	

(error in bond lengths ± ·04)

In the benzene ring the bond-length C–C average is 1·40, agreeing well with the value 1·41 Å observed by Robertson in the case of similar ring compounds. The length of the bond N–N = 1·27 is slightly greater than the value 1·23 given by Lange.[2] The angle N–N–C is 134° 30′. The planar benzene ring makes an angle of 42° 34′ with the (*ac*) planes. The plane of the ring is further tilted in the crystal, the tilt being nearly 10°. The bond-length between the methyl group carbon and the benzene carbon is 1·47 Å which is less than the usual value 1·51 reported in literature.

The nearest distance between the two molecules in the crystal is about 3·92 Å.

Summary

The crystal structure of *p*-azo-toluene has been determined by single crystal methods. The unit cell is monoclinic with $a = 12{\cdot}01$ Å, $b = 5{\cdot}02$ Å, $c = 9{\cdot}32$ Å, $\beta = 90° 12'$. The space-group is $P\,2_1/a - C_{2h}^5$ and there are two molecules per unit cell.

Atomic positions were determined by electron density projections making use of ' trial and error ' methods. Structure factors were obtained from visually estimated intensities on Weissenberg photographs taken with CuK_α radiation.

The planar benzene rings are attached by zig-zag C–N = N–C bond with the bond distance –N = N– = 1·27 Å and the angle N = N–C 134°

30′. The plane of the benzene ring makes an angle with the (*ac*) plane, its orientation is obtained by rotating it about the N–C bond by 10°. The nearest distance between two molecules in the crystal is 3·92 Å.

REFERENCES

1. Kapadia .. *Jour. Bombay Univ.*, 1938, **7**, 2.
2. Lange, Woodward and Robertson *Proc. Roy. Soc.*, 1939, **171 A**, 387.