Acta Cryst. (1970). B**26**, 889

The Crystal Structure of Benzalazine*

By U. C. Sinha†
Department of Physics, University of Allahabad, Allahabad, India

(*Received* 2 *January* 1968 *and in revised form* 23 *May* 1969)

The crystal structure of benzalazine, (C_6H_5–CH=N–)$_2$ has been determined by means of electron-density projections down two crystallographic axes. Atomic parameters have been refined by difference syntheses. The crystals are orthorhombic, space group *Pbcn* with $a=13{\cdot}09$, $b=11{\cdot}76$, $c=7{\cdot}62$ Å and four molecules per unit cell. The molecule is centrosymmetric and assumes a *trans* configuration. The $C_{aromatic}$– $C_{aliphatic}$ and N–N bonds are found to be shorter than the normal single bonds. The shortening of the C–C and N–N bonds is explained by the conjugation of the two C=N bonds with the benzene rings and the consequent contribution which an alternative excited structure makes to the normal state.

Introduction

The crystal structure analysis of benzalazine, C_6H_5–CH=N–N=CH–C_6N_5, was undertaken to determine the molecular conformation and the effect on the bond lengths of the molecule of conjugation involving the whole structure as indicated by ultraviolet absorption studies (Blout, Eager & Gofstein, 1946) and suggested by dipole moment measurements (Audrieth, Nespital & Ulich, 1933). The space group and preliminary structure have already been published (Sinha, 1959, 1961).

Experimental

Crystals of benzalazine, obtained by crystallization from solution in a mixture of chloroform and ethyl alcohol by slow evaporation of the solvent at room temperature, are yellow prisms elongated along the *c* axis. The density was determined by flotation in aqueous copper sulphate solution. Goniometric and X-ray studies of single crystals showed that the crystals were orthorhombic. Rotation and Weissenberg photographs were taken with Cu *Kα* radiation. The crystal and physical data are as follows:

C_6H_5–CH=N–N=CH–C_6H_5, M.W. 208·25, m.p. 92 °C
Orthorhombic
Axial lengths:

$$a=13{\cdot}09\pm0{\cdot}02\ \text{Å}$$
$$b=11{\cdot}76\pm0{\cdot}02$$
$$c=\ 7{\cdot}62\pm0{\cdot}01$$

These data were determined from high-angle reflexions in zero-layer Weissenberg photographs after application of a film shrinkage correction by Srivastava's method (1959) and using the method of Farquhar & Lipson (1946).

Density (by flotation) 1·178 g.cm^{-3}
Density (calculated) 1·177 g.cm^{-3}
Four molecules per unit cell.

Linear absorption coefficient for Cu *Kα* radiation, $\mu=6{\cdot}57$ cm^{-1}. Total number of electrons per unit cell, $F(000)=440$.

Systematic absences are consistent with the space group *Pbcn*. This space group requires eight asymmetric units to complete the necessary symmetry, but there are only four molecules in the unit cell. Hence a centre of symmetry must be ascribed to the molecule of benzalazine. The existence of the centre of symmetry is possible only when the central portion of the molecule is straight or has a *trans* configuration. This shows that the molecule cannot have a *cis* configuration.

The numbers of observed reflexions were: *hk*0, 98 out of 110 theoretically possible; *h*0*l*, 60 out of 64 possible; 0*kl*, 54 out of 62 possible.

Intensity measurements were made using the multiple-film technique, with the Moll recording microphotometer, and were put on the absolute scale by comparing 111, 220 and 311 reflexions of aluminum from a powder photograph of a mixture of benzalazine and aluminum in the ratio 8 to 1 by weight, the absolute intensity of the aluminum lines being taken from Brindley's (1936) measurements. These were corrected for the Lorentz and polarization factors. No attempt was made to correct for extinction or absorption errors, on account of the smallness of the crystals used (linear dimensions 0·2 to 0·4 mm) and the low coefficient of absorption. The structure amplitudes were derived by the usual formula for a mosaic crystal. Wilson's (1942) method was used to obtain the overall isotropic temperature factor. The overall temperature factor used for all the three zones was found to be 3·0 Å^2. Structure factors were calculated with the use of the atomic scattering factor curves of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for carbon and nitrogen.

Determination of the structure and refinement of atomic parameters

The relative shortness of the *c* axis and the nature of the intensity distribution of the 002 diffuse reflexion

---

* Taken from the thesis presented to the University of Allahabad (1961) in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Department of Physics.

† Present address: Department of Physics, Indian Institute of Technology, Powai, Bombay-76, India.

suggested that the orientation of the benzene ring would be about (001). The trial x and y coordinates were obtained from a consideration of certain outstandingly strong high-order $kh0$ reflexions, as was done for coronene by Robertson & White (1945). The structure was refined by the usual iterative process until all the structure factors stopped changing sign. The discrepancy index R was about 21·3%. The final (001) electron-density projection is shown in Fig. 1. Further refinement was carried out by three cycles of (001) difference syntheses and R decreased to 16·9%.

Since, in the calculation of the structure factors, contributions of hydrogen atoms were not considered, faint peaks were found at the probable hydrogen positions in the difference map, in addition to other spurious peaks. The hydrogen positions, obtained by assuming that they were situated on the diagonals of the benzene ring, with C–H = 1·08 Å, are shown in Fig. 2. The position of the hydrogen atom attached to C(1) was calculated on the basis of the difference map on (010). At this stage hydrogen atoms were also included in the calculation of structure factors. The improvement in the R value was found to be very small.

The features of importance in the (001) difference map are the peaks between C(3) C(4), C(4) C(5) and C(5) C(6) which are much sharper than the hydrogen

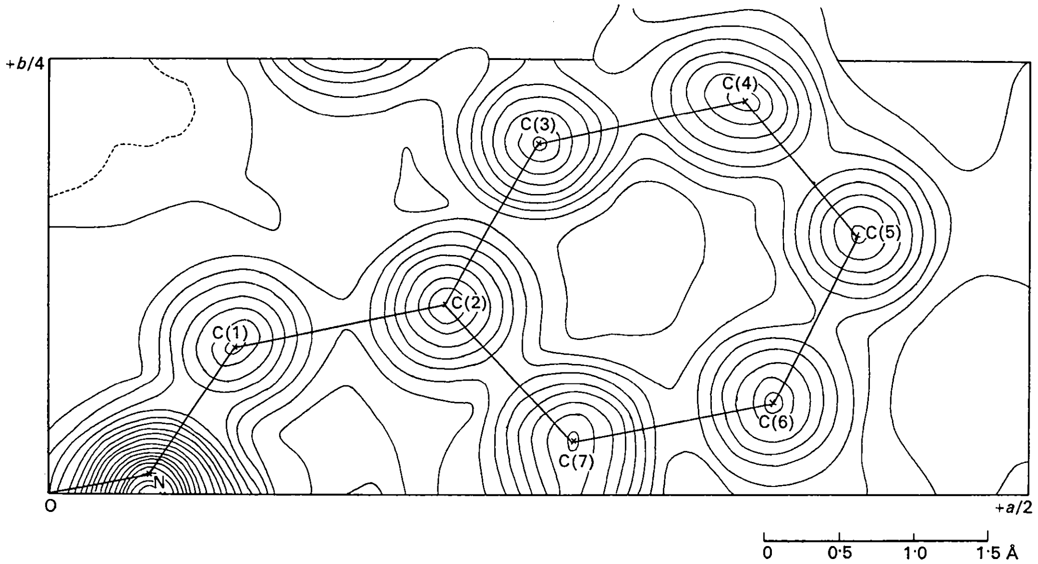

Fig. 1. Final (001) electron-density projection. Contours of intervals of 1 e.Å^{-2}. The zero-electron contour is broken.

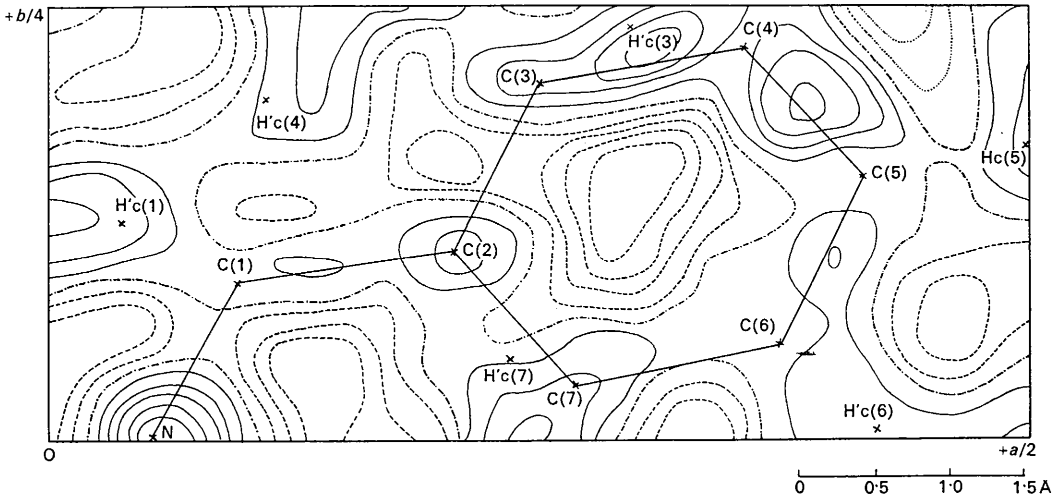

Fig. 2. Third (001) difference map. Contour interval, 0·25 e.Å^{-2}. Full lines: positive; chain lines: zero; broken lines: negative. Atomic positions after the second difference synthesis are marked. Calculated hydrogen positions are also marked.

peaks at assumed positions, and the depressions inside the benzene ring and at other places. Such peaks between the bonds and depressions inside the ring have been observed by Cruickshank (1956) in a detailed investigation of the structure of anthracene and these have been attributed to anisotropic thermal behaviour of the atoms. Hence, if anisotropic thermal parameters for different atoms are used, it is expected that the difference map will reveal the hydrogen atom positions more prominently, and the peaks along the bonds and the depressions will also tend to disappear. Such elaborate calculations were not undertaken.

The *z* coordinates were fixed by making an estimate of the angle of tilt between the molecule and (001). A choice between possible orientations of the N–N, C=N, C–C bonds and the benzene ring was made from packing considerations. In the (010) electron density projection the units at x, y, z and $\frac{1}{2}-x, \frac{1}{2}+y, z$ were found to overlap. However, on the resulting electron density map the position of the benzene skeleton was clearly indicated. The (010) projection was refined by the usual iterative process. *R* for $\{h0l\}$ was 25·5%. Further refinement of the *z* parameter was achieved by two cycles of difference syntheses and *R* decreased to 19·2%.

The refined *y* and *z* coordinates were used in the calculation of all observed $0kl$ reflexions: *R* was found to be 20·0%. On the resulting electron density projection on (100) there is much overlapping of the atoms of the asymmetric unit.

From the (001) and (010) difference maps (Figs. 2 and 3 respectively) it became evident that the different atoms had anisotropic thermal motions and even the isotropic temperature factor had been overestimated. The isotropic temperature factor variations were made by trial and error. It was assumed that all carbon atoms have more or less the same temperature factor and hence one value was used for all the carbon atoms. Finally the isotropic temperature factor *B* was taken to be 2·0 and 2·5 Å² for nitrogen and carbon respectively. Structure factors were calculated for all reflexions and *R* was found to be 12·2, 17·1 and 18·3% for $\{hk0\}$, $\{h0l\}$ and $\{0kl\}$ reflexions respectively, for observed reflexions only. The final atomic parameters are listed in Table 1, the origin being at the symmetry centre. The observed and calculated structure factors are given in Table 2.

Table 1. *Atomic coordinates*

	x	*y*	*z*
N	0·687 Å	0·000 Å	0·070 Å
C(1)	1·256	1·053	−0·332
C(2)	2·705	1·241	−0·189
C(3)	3·273	2·402	−0·699
C(4)	4·616	2·681	−0·521
C(5)	5·428	1·782	0·185
C(6)	4·862	0·643	0·681
C(7)	3·510	0·363	0·517

The bond lengths and angles are listed in Table 3 and shown in Fig. 4.

The equation of the least-squares plane of the carbon atoms of the asymmetric unit is

$$3{\cdot}3624x-8{\cdot}3134y-14{\cdot}6921z=1\ .$$

The maximum and minimum deviations of the atoms from the plane are 0·038 and 0·000 Å respectively. The molecules are grouped in a zigzag way in space in the unit cell. The N–N bond makes an angle of 5°49′ with (001), 5°49′ with the *a* axis and 90° with the *b* axis. The inclination of the line joining C(1), C(2), C(5) with (001) is 6°40′, whereas the benzene ring is rotated about C(3), C(6) in such a way that its inclination to (001) is 30°12′. The nitrogen atoms are rotated out of the planes formed by carbon atoms in such a way that the molecule is centrosymmetric and assumes a *trans* configuration. The benzene rings and atom C(1) of a molecule are coplanar.

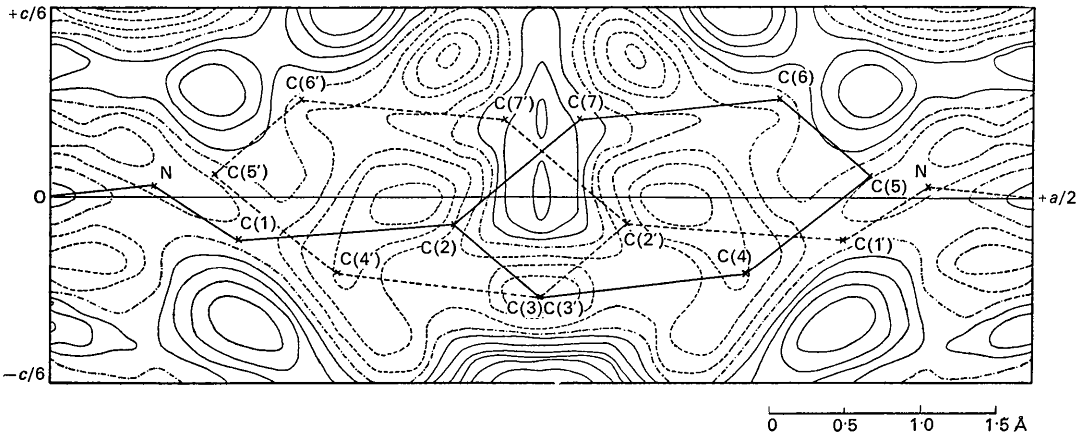

Fig. 3. Second (010) difference map. Contour interval, 0·25 e.Å⁻². Full lines: positive; chain lines: zero; broken lines: negative. Atomic positions after the first difference synthesis are marked.

Table 2. *Observed and calculated structure factors*

Within each group the columns, reading from left to right, contain the values of *h*, *k* or *l*, $10F_o$ and $10F_c$.

k		
	0*k*0	
2	554	601
4	417	386
6	31	−29
8	137	123
10	207	179
12	33	−27
14	23	40
	1*k*0	
1	294	312
3	547	551
5	137	−126
7	178	147
9	266	272
11	290	300
13	10	13
15	23	26
	2*k*0	
0	556	−582
2	393	376
4	189	−163
6	361	324
8	189	146
10	62	−55
12	236	223
14	83	92
	3*k*0	
1	413	392
3	419	384
5	508	508
7	78	−56
9	10	−7
11	148	−118
13	78	81
	4*k*0	
0	196	−176
2	137	101
4	267	238
6	318	299
8	95	62
10	172	191
12	117	−102
14	32	−37
	5*k*0	
1	188	118
3	351	−313
5	146	−90
7	146	105
11	74	−91
13	35	−11
	6*k*0	
0	751	−707
2	308	−239
4	53	75
6	279	−232
8	67	41
10	101	−78
14	35	−45

k		
	7*k*0	
1	378	−324
3	129	−113
5	58	48
7	153	184
9	182	−195
11	57	−64
13	21	−33
	8*k*0	
0	207	147
2	201	−140
4	122	126
6	123	−143
8	252	−262
10	63	−91
12	103	−118
	9*k*0	
1	249	−224
3	321	−330
5	277	−256
7	161	−182
9	68	58
	10*k*0	
0	122	−137
2	44	45
4	413	441
6	168	−160
8	29	−29
10	24	−36
12	35	40
	11*k*0	
1	63	89
3	87	63
5	95	−105
7	192	−212
9	51	−38
11	41	−52
	12*k*0	
0	45	31
2	191	−214
4	55	−41
8	46	−48
10	26	−25
	13*k*0	
1	141	−148
5	54	−62
7	54	−52
9	44	−64
	14*k*0	
0	30	22
6	10	−17
8	24	43
	15*k*0	
5	14	35
7	54	68
	16*k*0	
4	53	55

h		
	*h*02	
0	2131	2192
1	228	217
2	77	−87
3	201	−206
4	83	−119
5	80	18
6	547	−474
7	23	28
8	82	−86
9	55	−21
10	25	−26
11	38	−84
12	35	21
13	74	92
14	29	29
15	21	20
16	19	−26
	*h*04	
0	250	347
1	108	162
2	358	361
3	44	−54
4	20	−60
5	169	−111
6	114	−150
7	52	49
8	304	−308
9	63	−58
10	126	124
12	41	−28
13	58	61
14	23	30
15	22	36
	*h*06	
0	111	−119
1	59	76
2	118	269
5	148	−162
6	32	−41
7	47	28
8	220	−280
9	49	−61
10	71	115
11	60	86
12	29	−27
	*h*08	
0	37	−49
1	48	42
2	22	135
3	22	24
4	26	10
5	48	−91
6	30	−35
7	24	−12
8	52	−102
9	25	−45

l		
	02*l*	
1	120	57
2	464	513
3	180	102
4	253	275
5	123	97
6	62	134
7	83	76
8	21	47
9	41	42
	04*l*	
1	337	−335
2	20	82
3	402	−405
4	227	−173
5	10	−16
6	162	−166
7	164	219
8	34	−42
9	59	−131
	06*l*	
1	34	−17
2	55	51
3	50	−46
4	100	136
5	58	−55
6	73	114
7	51	−38
8	43	81
	08*l*	
1	246	−248
2	163	178
3	415	−441
4	207	262
5	228	−325
6	114	153
7	36	−88
8	27	40
	010*l*	
1	11	23
2	135	137
3	16	30
4	84	116
5	27	−5
6	36	68
7	12	−27
	012*l*	
4	53	125
6	45	113

Table 3. *Bond lengths and angles*

	Bond length		Bond angle
N—N′	1·380 Å	N′—N—C(1)	115·0°
C(1)-N	1·264	N—C(1)-C(2)	122·5
C(1)-C(2)	1·465	C(1)-C(2)-C(3)	119·0
C(2)-C(3)	1·389	C(3)-C(2)-C(7)	118·6
C(3)-C(4)	1·383	C(2)-C(3)-C(4)	121·2
C(4)-C(5)	1·402	C(3)-C(4)-C(5)	120·0
C(5)-C(6)	1·365	C(4)-C(5)-C(6)	118·8
C(6)-C(7)	1·390	C(5)-C(6)-C(7)	122·0
C(7)-C(2)	1·385	C(6)-C(7)-C(2)	119·6
		C(7)-C(2)-C(1)	122·0

The standard deviations in atomic coordinates were estimated by the formula of Cruickshank (1949) and are given in Table 4. The corresponding mean standard deviations in the bond lengths are 0·018 Å for C–C (benzene ring), 0·018 Å for $C_{aromatic}$–$C_{aliphatic}$, 0·017 Å for C=N and 0·014 Å for N–N.

Table 4. *Standard deviations*

	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
N	0·008 Å	0·008 Å	0·014 Å
C(1)	0·009	0·01	0·018
C(2)	0·009	0·01	0·018
C(3)	0·009	0·009	0·016
C(4)	0·01	0·01	0·018
C(5)	0·01	0·01	0·018
C(6)	0·01	0·01	0·019
C(7)	0·009	0·009	0·016

The causes of the persistently high value of *R* for the {010} and {100} zones may be:

(i) the small average value of the observed structure factors in these zones, because the accuracy of measurement of a low-intensity reflexion is much less compared with that of higher-intensity reflexions;

(ii) the fact that isotropic temperature factors were used and these are not well suited to these zones because of the anisotropic thermal motion of the atoms;

(iii) small errors in the *z* coordinates because of overlapping of the atoms in the (010) projection.

The individual C–C distances in the benzene ring do not differ significantly from the mean value of 1·39 Å. The bond angles in the benzene ring are also quite normal, their values lying in the range between 118·6 and 122° with an average value of 120°.

The C(1)–C(2) bond in benzalazine is found to be 1·465 Å, which is less than the value of 1·51 Å found in toluene for a single C–C bond between an aromatic carbon atom and an aliphatic carbon atom (Robertson, 1953). It is, however in good agreement with values usually reported for a single C–C bond between an aromatic carbon atom and aliphatic carbon atom between a double bond and a benzene ring; *e.g.* in stilbene the C–C distance is 1·44 Å (Robertson & Woodward, 1937). This shortening of the C–C bond may therefore be regarded as being due to conjugation between the benzene ring and C=N. The C–C bond in benzalazine between the benzene nucleus and a double bond (C=N), corresponds to 15% double-bond character (Pauling, 1960).

The N–N single bond in benzalazine is 1·38 Å, which is considerably smaller than the N–N single-bond value of 1·47 Å found in an electron diffraction study of the N_2H_4 gas molecule by Giguère & Schomaker (1943) and 1·46 Å found by Collin & Lipscomb (1951) in an X-ray investigation of solid N_2H_4. It should be pointed out however that the nature of the bond in the present case is entirely different from that in the case of N_2H_4. It was thought that the low value of the N–N bond might be due to a slight inaccuracy in the measurement of the *z* parameter, but the change is so significant that it cannot be accounted for in this way, as the estimated standard deviation for the N–N bond is only 0·014 Å. This indicates that the N–N bond has some double-bond character. Ultraviolet absorption studies indicate the existence of conjugated resonating systems. There is thus no doubt that the ordinary formula for benzal-

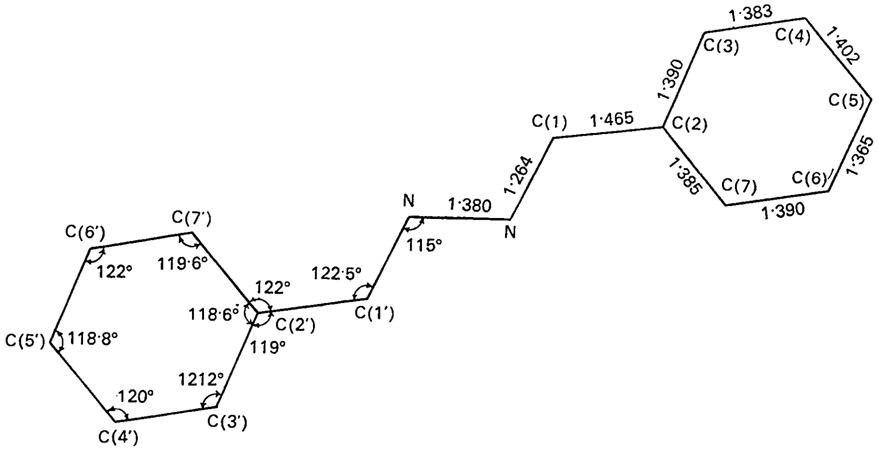

Fig. 4. Observed bond lengths and angles.

azine [Fig. 5(*a*)] does not represent the molecule completely, and that an excited structure of the form represented by Fig. 5(*b*) must also contribute to the normal state. In Fig. 5(*b*) the dots in the *para* positions represent single electrons, which can be formally considered as paired. Such formula have been discussed by Robertson & Woodward (1937) in relation to the structure of stilbene. The coplanarity of the molecule also supports the existence of structure (*b*) (Ingold, 1953). In addition the correlation between resonance and colour in organic substances affords an explanation of these results (Hückel, 1958). The yellow colour of benzalazine may be attributed to transitions to excited states (Syrkin & Dyatkina, 1964). It is thus concluded that in the actual structure there is resonance between the forms (*a*) and (*b*).

The C=N bond is found to be 1·264 Å which is not significantly different from the expected value of 1·27 Å; the difference is within the limits of experimental error. The C=N bond in dimethylglyoxime as found by X-ray analysis is 1·27 Å (Merritt & Lanterman, 1952) and by neutron diffraction studies, 1·253 Å (Hamilton, 1961).

These considerations show that the molecule of benzalazine has a *trans* configuration with conjugation involving the two C=N bonds and the benzene rings, in agreement with the ultraviolet absorption studies, which indicate extensive conjugation involving the whole molecule. As a result of these conjugations, the C(1)–C(2) and N–N bonds are found to possess some double-bond character.

The intermolecular packing arrangements can be seen in Figs. 6 and 7 which give the unit cell of the structure projected down [001] and [010] respectively. Molecules are grouped in a zigzag way in space with the planes of the benzene rings in alternate layers (nearest) being inclined to one another at an angle of 60·4°. All the intermolecular distances correspond to normal van der Waals interactions. The nearest distance between the non-bonded carbon atoms C(7) of the unit at *xyz* and C(7) of the unit at $x, \bar{y}, \frac{1}{2}+z$ is 3·88 Å. The distance between the non-bonded nitrogen atoms is 3·81 Å.

All computations were carried out with the help of a Remington Rand Printing Table Calculating Machine. All syntheses were carried out with the help of Beevers–Lipson strips at 3° intervals prepared in this laboratory. The author is much indebted to Professor K. Banerjee for his valuable guidance and encouragement throughout the progress of the work and his thanks are due to Dr S. C. Chakraborty for his continued interest and help. Finally he wishes to express his thanks to the Ministry of Education, Government of India, for financial assistance in the form of a scholarship.

References

Audrieth, L. E., Nespital, W. & Ulich, H. (1933). *J. Amer. Chem. Soc.* **56**, 673.

Berghuis, J., Haanappel, IJ. M., Potters, M., Loopstra, B. D., MacGillavry, C. H. & Veenendaal, A. L. (1955). *Acta Cryst.* **8**, 478.

Blout, E. R., Eager, V. W. & Gofstein, R. M. (1946). *J. Amer. Chem. Soc.* **68**, 1983.

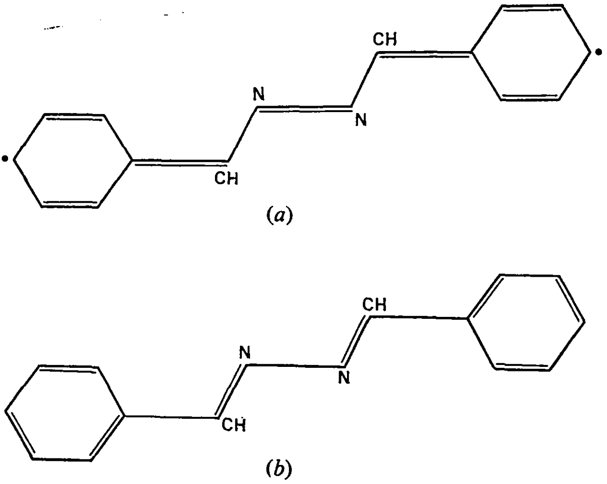

Fig. 5. (*a*) Normal structure, (*b*) excited structure.

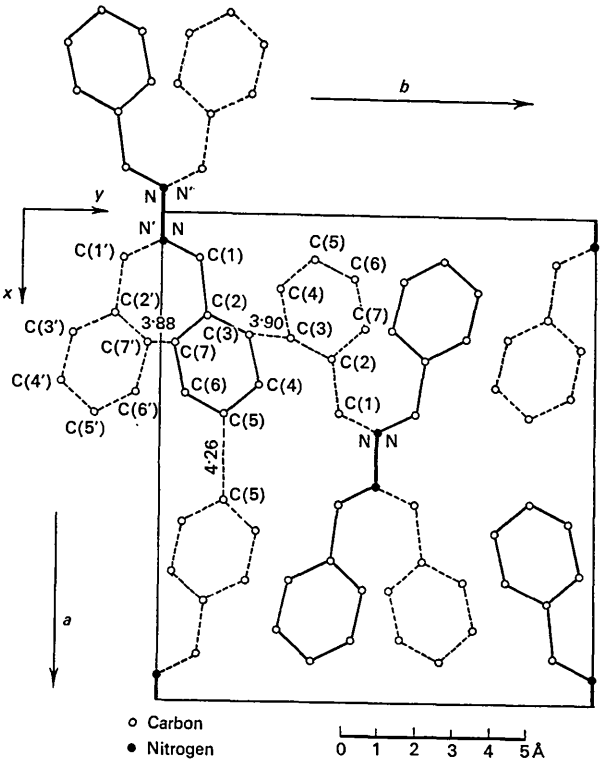

Fig. 6. The structure projected down [010].

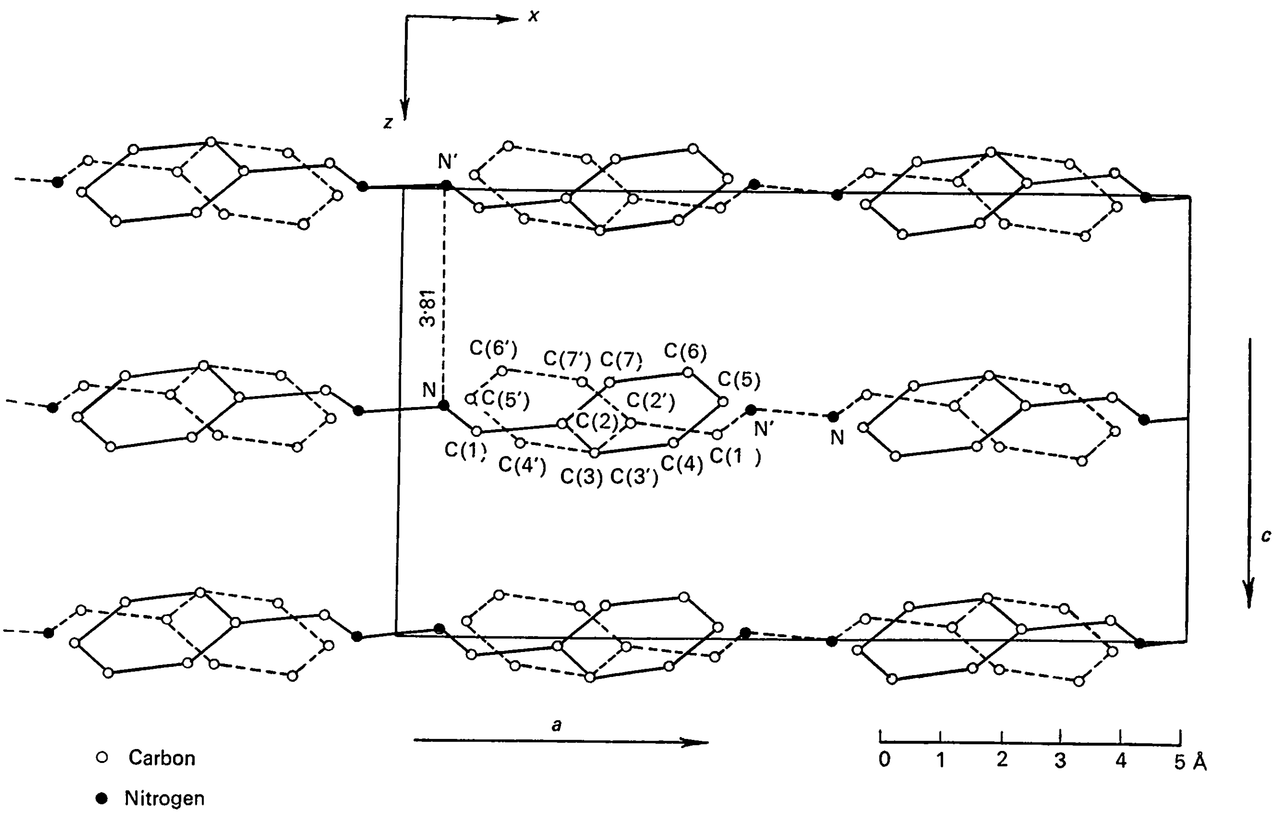

Fig. 7. The structure projected down [010].

Brindley, G. W. (1936). *Phil. Mag.* **21**, 778.

Collin, R. L. & Lipscomb, W. N. (1951). *Acta Cryst.* **4**, 10.

Cruickshank, D. W. J. (1949). *Acta Cryst.* **2**, 65.

Cruickshank, D. W. J. (1956). *Acta Cryst.* **9**, 915.

Farquhar, M. C. M. & Lipson, H. (1946). *Proc. Phys. Soc. Lond.* **58**, 200.

Giguère, P. A. & Schomaker, V. (1943). *J. Amer. Chem. Soc.* **65**, 2025.

Hamilton, W. C. (1961). *Acta Cryst.* **14**, 95.

Hückel, W. (1958). *Theoretical Principles of Organic Chemistry*, Vol. II, p. 640. Elsevier Publishing Co.

Ingold, C. K. (1953). *Structure and Mechanism in Organic Chemistry*, p. 147. Ithaca: Cornell Univ. Press.

Merritt, Lynne, L. Jr & Lanterman, E. (1952). *Acta Cryst.* **5**, 811.

Pauling, L. (1960). *The Nature of the Chemical bond*, p. 235. Ithaca: Cornell Univ. Press.

Robertson, J. M. (1953). *Organic Crystals and Molecules*, p. 182. Ithaca: Cornell Univ. Press.

Robertson, J. M. & White, J. G. (1945). *J. Chem. Soc.* II, p. 607.

Robertson, J. M. & Woodward, I. (1937). *Proc. Roy. Soc. Lond.* A **162**, 568.

Sinha, U. C. (1959). *Bull. Nat. Inst. Sci. India*, **14**, 107.

Sinha, U. C. (1961). *Indian J. Phys.* **35**, 374.

Srivastava, S. N. (1959). *Acta Cryst.* **12**, 412.

Syrkin, Y. K. & Dyatkina, M. E. (1964). *Structure of Molecules and the Chemical Bond*, p. 450 New York: Dover Publications.

Wilson, A. J. C. (1942). *Nature, Lond.* **150**, 152.