Acta Cryst. (1955). 8, 224

The Crystal and Molecular Structure of *s*-Triazine

By P. J. Wheatley*

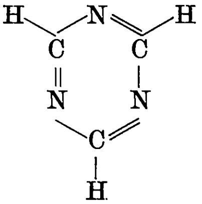
School of Chemistry, University of Minnesota, Minneapolis 14, *U.S.A.*

(*Received* 4 *December* 1954)

A three-dimensional structure analysis of *s*-triazine is described. The molecule is planar but deviates quite markedly from a regular hexagon. The C–N distance is 1·319 Å, with a standard deviation of 0·005 Å. The C–H distance is 1·00 Å. The N–C–N angle is 126·8° and the C–N–C angle is 113·2°, each with a standard deviation of 0·4°. The final R factor for the 97 observed reflexions, excluding two which are strongly extinguished, is 7·2%.

Introduction

s-Triazine (I) is an interesting molecule from many points of view.



(I)

Calculations by Pauling & Sturdivant (1937) suggested that the molecule should be stable, but it is only recently that Grundmann & Kreutzberger (1954) have characterized the substance. Recent work by Cox & Smith (1954) and by Stoicheff (1954) on benzene seem to show a significant difference between the C–C distance in the solid and vapour phases. *s*-Triazine is a comparable molecule for which the rotational Raman lines might be resolved, and it would be interesting to see if a discrepancy similar to that indicated for benzene occurs. The calculations of Pariser & Parr (1953) on the azines assume that the molecules are regular hexagons, although work on pyridine (DeMore, Wilcox & Goldstein, 1954) and pyrazine (Schomaker & Pauling, 1939) indicates that this is not strictly true. The accumulation of accurate data for the azines might lead to a more refined theory of the heteroatomic analogues of benzene, and it is intended that this paper should be the first of such a series. Finally, some doubt exists as to the order/length curve for C–N bonds. A reliable bond length can be ascribed to the C–N single bond, and the work of Hughes (1941) on melamine gives a second point if all the C–N bonds are assumed to have one-third double-bond character. The present molecule, where the bonds may be assumed to have one-half double-bond character, carries the curve a little further towards the elusive double-bond point.

Experimental

The space group and molecular configuration of *s*-triazine have been determined by Siegel & Williams (1954). At the time their letter was published, all the three-dimensional data had been collected for the present investigation, and Siegel & Williams were kind enough to suggest that this investigation should be completed.

The systematic absences noted by Siegel & Williams were confirmed and extended, characterizing the space group as $R\bar{3}c$. The unit-cell dimensions, determined from Straumanis photographs, are

$$a = 9{\cdot}647 \pm 0{\cdot}003,\ c = 7{\cdot}281 \pm 0{\cdot}003\ \text{Å}\,.$$

These figures yield a calculated density of 1·376 g.cm.$^{-3}$, which may be compared with a value of 1·367 g.cm.$^{-3}$ obtained by flotation. Cu $K\alpha$ radiation and the multiple-film technique were employed to take Weissenberg photographs round [a] and [c]. Despite the fact that the melting point of *s*-triazine is 85° C., the crystals sublime rapidly at room temperature, and hence a high vapour pressure must be maintained round the crystals. For the photographs round [a], a crystal grown from the melt in Lindemann glass tube of 0·3 mm. internal diameter was employed. For those round [c] a crystal grown by sublimation and mounted inside a thin-walled Pyrex bulb was used.

The relative intensities were estimated visually by comparison with a standard chart, and the intensities from the different sets of photographs were placed on the same relative scale by correlation through common reflexions. A total of 97 independent reflexions were observed.

The X-ray structure analysis

The asymmetric unit consists of one C, one H and one N atom, and the fact that the molecule lies in a special position fixes the y and z coordinates for each atom. Thus the only parameters to be determined are the three x coordinates, which measure the distance of each atom from the centre of the ring. Structure fac-

---

* On leave of absence from the Department of Inorganic and Structural Chemistry, The University, Leeds 2, England.

tors were calculated for the *hki*0 and *h*0$\bar{h}$*l* planes, on the assumption that the C–N distance was 1·34 Å and that all angles were 120°. An *R* factor of $\sim 20\%$ was obtained, and there were immediate indications that strong thermal anisotropy was present, the direction of maximum thermal motion being perpendicular to the plane of the ring. Calculation of the $\bar{h}$*kil* structure factors showed very poor agreement and it was obvious that the x coordinates of the C and N atoms were not the same. Reference to the work of Hughes (1941) and Wiebenga (1952) was of little help as their results are in the opposite sense. However, trial calculations with the $\bar{h}$*kil* planes soon showed that the present case was similar to melamine, with the C atom nearer to the centre of the ring than the N atom. As soon as this had been established the structure could rapidly be refined by successive (F_o-F_c) syntheses along the line $(x, 0, \frac{1}{4})$ using all the three-dimensional data.

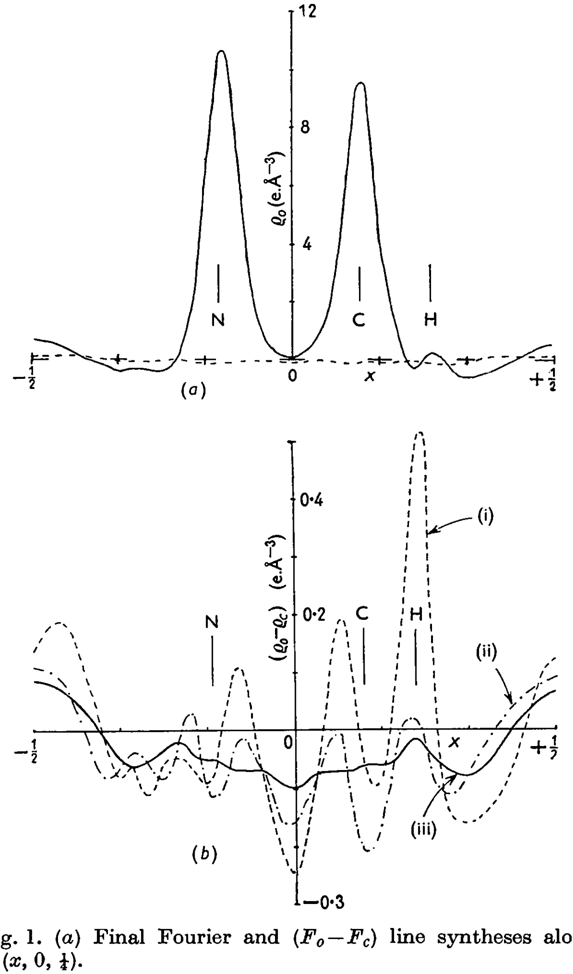


Fig. 1. (*a*) Final Fourier and (F_o-F_c) line syntheses along $(x, 0, \frac{1}{4})$.
(*b*) Three stages in the refinement, illustrated by difference maps. (i) Before the contribution from the H atom is included in the calculated structure factors. Slight shifts are still needed in the C and N atoms. (ii) After refinement of the atomic parameters, but showing that the thermal factors for the C and N atoms are still too small. (At this stage values of $A = 3{\cdot}9$ Å^2 and $B = 4{\cdot}0$ Å^2 were being used for each atom.) (iii) Final difference map.

The scattering factors used for the C and N atoms were those recently calculated by Hoerni & Ibers (1954), and that for H was taken from the computations of McWeeny (1951). After the atomic positions had been decided, it was necessary to refine the temperature factors. To allow for thermal anisotropy the equation quoted by Hughes (1941) was used:

$$f = f_0 \exp\left[-(A+B\cos^2\varphi)(\sin^2\theta/\lambda^2)\right],$$

where φ is the angle between the normal to the reflecting plane and the direction of maximum vibration, in this case [*c*]. The final choice of A and B for the for the C and N atoms is shown in Table 1. The same values were used for the H atom as were used for the C atom, and there is some indication in the final difference map that these values should, as expected, be increased slightly for the H atom. Fig. 1(*a*) shows the final Fourier and difference maps on the same scale, and Fig. 1(*b*) some of the difference maps, on a larger scale, as the refinement progressed.

Table 1. *A and B values*

Atom	A (Å^2)	B (Å^2)	$(A+B)$ (Å^2)
C	4·4	4·2	8·6
N	4·0	4·2	8·2

The final parameters and molecular dimensions are shown in Table 2. Fig. 2 shows the arrangement of the molecules in the unit cell. In Fig. 2(*a*) the molecules are viewed down [*c*] and in Fig. 2(*b*) in a direction perpendicular to [*c*] and parallel to the short diagonal of the basal plane, in order to show the stepwise packing along the long diagonal. The molecules are separated by $\frac{1}{2}c$, i.e. 3·64 Å, in one direction. Along the stepwise formation, the shortest distances between non-bonded atoms are C · · · C, 3·31 Å; N · · · N, 3·17 Å.

Table 2. *Final parameters and and molecular dimensions*

Atom	x (Å)
C	1·2715
N	−1·3622
H	2·269

Bond	Length (Å)	Angle (°)	
C–N	1·319	N–C–N	126·8
C–H	0·998	C–N–C	113·2

An assessment of the accuracy of the analysis was made in the manner described by Cruickshank (1949) and Cruickshank & Rollett (1953), the curvature of the peaks being estimated from the final Fourier map. These calculations yielded a standard deviation of the x coordinate of the C and N atoms of about 0·004 Å. Since the positions of the atoms can vary only along the x direction, this figure gives a rather low value for the standard deviation of the C–N bond length of 0·005 Å. The standard deviation of the angles is about 0·4°.

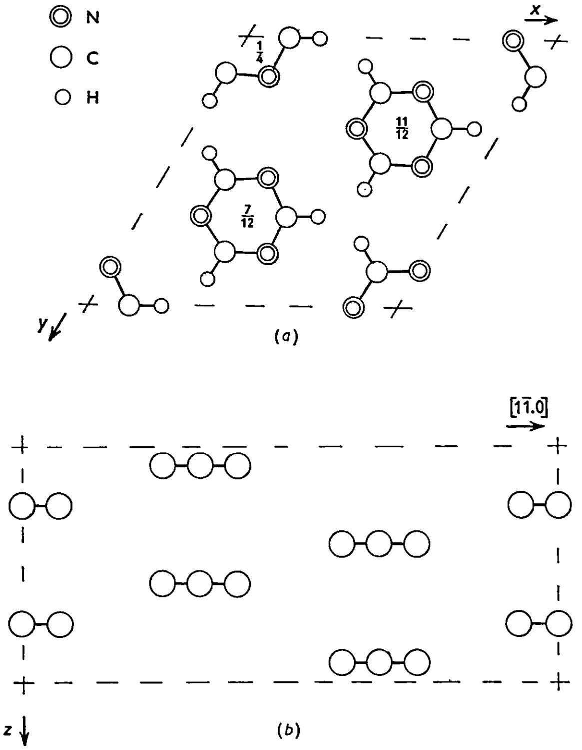


Fig. 2. (*a*) *s*-Triazine: projection on (0001). Beneath each molecule in this projection is another, rotated by 60°, and separated from the one above by $\frac{1}{2}c$. Figures denote height above the origin in the *z* direction.

(*b*) *s*-Triazine: idealized diagram showing nature of stacking along [1$\bar{1}$.0]. The H atoms are omitted.

Two of the planes, 11$\bar{2}$0 and 01$\bar{1}$2, were strongly extinguished, and these were included in the Fourier and difference syntheses with their calculated values. If these two planes are omitted when obtaining the reliability factor, and only observed structure factors are considered, the final *R* factor is 7·2%.

Discussion of the structure

The most noticeable feature of these results is the deviation of the molecule from a regular hexagon. The assumption that the molecule is a regular hexagon implies that both the C and N atoms are trigonally hybridized. The present analysis shows, however, that there is considerable departure from pure sp^2 hybridisation, in opposite senses for the C and N atoms, and these deviations may be expected to show in various ways when the properties of this molecule are studied more closely.

The C–N distance of 1·319 Å corresponds, on the resonance picture, to 50% double-bond character. In Fig. 3 an order/length curve for C–N bonds is plotted and compared with the corresponding curve for C–C bonds (Pauling, 1940). The single-bond distance is the value given by Cox & Jeffrey (1951) from a survey of many experimental values. The value at one-third double-bond character is from melamine (Hughes, 1941). If the C–N curve is assumed to have the same general shape as the C–C curve, these points extrapolate to give a value of 1·28 Å for the C–N double-bond distance.

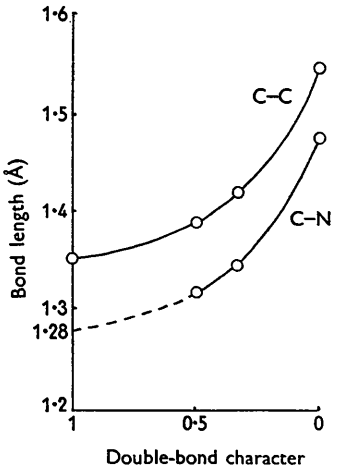


Fig. 3. Order/length curves for C–C and C–N bonds.

I would like to extend my thanks to Prof. E. G. Cox of the University of Leeds, in whose department the experimental part of this work was performed; to the members of the Department of Chemistry of the University of Minnesota for their hospitality whilst the refinement progressed; and to Dr R. Pariser of the Jackson Laboratories of E. I. du Pont de Nemours and Co., who kindly provided the sample of *s*-triazine.

References

Cox, E. G. & Jeffrey, G. A. (1951). *Proc. Roy. Soc.* A, **207**, 110.

Cox, E. G. & Smith, J. A. S. (1954). *Nature, Lond.* **173**, 75.

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

Cruickshank, D. W. J. & Rollett, J. S. (1953). *Acta Cryst.* **6**, 705.

DeMore, B. B., Wilcox, W. S. & Goldstein, J. H. (1954). *J. Chem. Phys.* **22**, 876.

Grundmann, C. & Kreutzberger, A. (1954). *J. Amer. Chem. Soc.* **76**, 632.

Hoerni, J. A. & Ibers, J. A. (1954). *Acta Cryst.* **7**, 744.

Hughes, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737.

McWeeny, R. (1951). *Acta Cryst.* **4**, 513.

Pariser, R. & Parr, R. G. (1953). *J. Chem. Phys.* **21**, 767.

Pauling, L. (1940). *The Nature of the Chemical Bond.* Ithaca: Cornell University Press.

Pauling, L. & Sturdivant, J. H. (1937). *Proc. Nat. Acad. Sci., Wash.* **23**, 615.

Schomaker, V. & Pauling, L. (1939). *J. Amer. Chem. Soc.* **61**, 1769.

Siegel, L. A. & Williams, E. F. (1954). *J. Chem. Phys.* **22**, 1147.

Stoicheff, B. P. (1954). *Canad. J. Phys.* **32**, 339.

Wiebenga, E. H. (1952). *J. Amer. Chem. Soc.* **74**, 6156.