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Apparent Molecular Rotation in Cycl(3,2,2)azine

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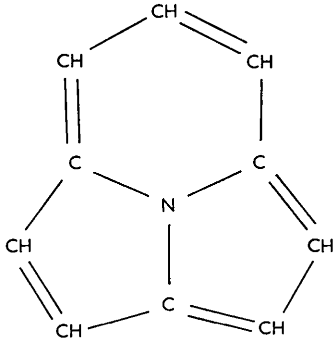
The tetragonal phase of cycl(3,2,2)azine ($I4_1cd$, $a=7{\cdot}58$, $c=26{\cdot}81$ Å, $Z=8$) is metastable at room temperature, and changes spontaneously into a monoclinic phase

$$(Ia \text{ or } I2/a,\ a=20{\cdot}74,\ b=7{\cdot}35,\ c=20{\cdot}65 \text{ Å},\ \beta=101{\cdot}0°,\ Z=16)\ .$$

A three-dimensional analysis of the tetragonal phase indicates that the molecules either rotate relatively freely in their respective planes, or are randomly oriented in these planes. An analysis of the monoclinic phase has not been attempted, but consideration of the apparent temperature factor suggests that rotation (or random orientation) of the molecules occurs in this phase also.

Introduction

Cycl(3,2,2)azine ($C_{10}H_7N$) is a stable aromatic compound synthesized by Windgassen, Saunders & Boekelheide (1959). A crystal-structure analysis was undertaken in this laboratory in order to study the stereochemistry and packing of the molecules. It will be seen that the unusual nature of the crystal structure prevents any detailed study of the molecule.



Experimental details

Although its melting point is 65 °C., cycl(3,2,2)azine is inconveniently volatile at room temperature. Moreover, the crystals in the available sample were rather small, and an attempt was therefore made to grow single crystals from the melt in a sealed, thin-walled glass capillary. The attempt was not successful; the liquid would supercool almost to room temperature and then crystallize abruptly as an unsuitable aggregate. However, it was found that if the capillary were then maintained for several days at a temperature of 63 °C. (that is, 2 °C. below the melting point), excellent single crystals were formed. These were randomly-oriented and contiguous, and many were large enough to permit single-crystal X-ray examination without serious interference from their neighbours. Crystal boundaries were easily located by optical examination.

Sometimes the crystals so formed were monoclinic, and apparently completely stable. More often, however, they were tetragonal, and metastable at room temperature. Upon cooling, and after an interval of several minutes to a week or more, the tetragonal crystals would spontaneously change into a crystalline aggregate, identifiable by powder photography as the monoclinic phase. This change (which the author has twice seen actually occurring on the stage of a polarizing microscope) is rapid and complete. A disturbance can be seen travelling along the sample, heedless of individual crystal boundaries, transforming the transparent, variously oriented single crystals into a translucent mass in which optical extinctions can no longer be observed. The rate of travel of the disturbance, in a capillary of 0·5 mm. diameter, is estimated to be about 0·3 mm.sec.$^{-1}$.

The crystal data for the two forms are as follows:

Stable phase:

Monoclinic, Ia or $I2/a$.

$a=20{\cdot}74\pm0{\cdot}02$, $b=7{\cdot}35\pm0{\cdot}02$, $c=20{\cdot}65\pm0{\cdot}02$ Å; $\beta=101{\cdot}0\pm0{\cdot}1°$.

D_x (calculated density) $=1{\cdot}214\pm0{\cdot}005$ g.cm.$^{-3}$ ($Z=16$).

D_o (observed density) $=1{\cdot}21\pm0{\cdot}03$ g.cm.$^{-3}$.

Metastable phase:

Tetragonal, $I4_1cd$.

$a=7{\cdot}58\pm0{\cdot}03$, $c=26{\cdot}81\pm0{\cdot}11$ Å.

$D_x=1{\cdot}22\pm0{\cdot}02$ g.cm.$^{-3}$ ($Z=8$).

D_o could not be determined, but probably is not much different from the value obtained for the stable phase.

For both phases:

$\mu=6{\cdot}8$ cm.$^{-1}$ (Cu $K\alpha$).

The space groups were deduced from examination of Weissenberg and precession photographs. The cell constants of the tetragonal phase were measured from precession photographs, while those of the monoclinic phase were measured with the General Electric XRD5 spectrogoniometer and goniostat.

Three-dimensional intensity data for the tetragonal phase were obtained from a cylindrical crystal of diameter 0·5 mm., for which **a** was nearly coincident with the capillary axis. The data were recorded on zero- and upper-level x-axis Weissenberg photographs (using Cu $K\alpha$ radiation), and estimated visually by comparison with a standard wedge. Data for different levels were correlated by means of a double-slit technique, and abundant additional correlations were provided by the high symmetry of the reciprocal lattice.

While absorption should have been negligible for this crystal, there was evidence that extinction was not. Actual splitting of the two strongest reflections was observed on some films; presumably the extinction for these reflections was so great that effectively only the edges of the crystal could contribute. It seems likely that the conditions of crystal growth were responsible for an unusual degree of perfection and consequent extreme extinction effects. In order to reduce errors from this source, a supplementary set of data was obtained from a second crystal, of diameter 0·2 mm. (mounted this time about [110]). Attempts to grow still smaller crystals were unsuccessful; for some reason only monoclinic crystals were found in the smallest capillaries.

Appropriate Lorentz-polarization factors (for a mosaic crystal) were applied, and, where necessary, corrections were made for the distortion of spots on upper-level photographs. About 438 independent reflections were accessible on the Weissenberg photographs, and of these, 191 were observed. The range of observed amplitudes is about 1 to 110.

The diffraction pattern of the tetragonal crystal includes some strong diffuse streaks. These surround the more intense reflections, and tend to form bridges between them, frequently passing through the sites of systematically-absent reflections.

Three-dimensional intensity data for the monoclinic phase were obtained from a cylindrical crystal of diameter 0·1 mm., for which **b** was almost precisely parallel to the cylinder axis. The intensities were measured with the General Electric XRD5 spectrogoniometer and goniostat, using the 'moving-crystal–moving-counter' technique (Furnas, 1957). Cu $K\alpha$ radiation, and a General Electric SPG1 (argon-filled) counter tube were used. The combination of a nickel filter and a reverter (a form of pulse-height analyser) provided effectively monochromatic response. The only reciprocal-lattice points scanned were those for which the Bragg angle was less than 45°, as an examination of Weissenberg films indicated that no significant scattering would be observed at higher angles. Only limited use has been made of these data.

The total mosaic spread has been measured for this crystal, and is about 0·05°. It does seem that the conditions of crystal growth favour an unusual degree of perfection.

Structure determination of the tetragonal phase

Since there are sixteen general positions in the unit cell, and only eight molecules, it is clear that the latter must make use of the diad axes. Moreover, since the space group lacks a centre, the z coordinate of the molecule is arbitrary. Given a reasonable molecular model, therefore, only the angle between the molecular plane and **a** is needed to specify the approximate structure. A three-dimensional Patterson synthesis indicated a value of about $22\frac{1}{2}$° for this angle, and appropriate structure factors were calculated. The agreement with the observed structure amplitudes was surprisingly poor, however, and no refinement techniques served to reduce the agreement residual ($R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$) below about 0·40.

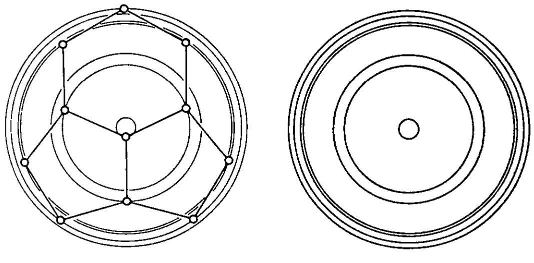


Fig. 1. Derivation of the rotating molecule.

At this point an X-ray analysis of the 1,4-dibromo derivative was undertaken (Hanson, 1961), and when this analysis confirmed the assumed molecular model, it was realized that the crystal structure must be of an unorthodox character. Two curious phenomena were considered next. It had been observed that the X-ray intensities fell off very rapidly with increasing Bragg angle, suggesting unusual thermal activity. Also, although there was in the Patterson synthesis a well-defined plane of intramolecular vectors, there were literally no resolved peaks (except that at the origin) within this plane, and thus, apparently, no specific intramolecular vectors in the structure. Both these phenomena are consistent with a structure in which the molecules rotate more or less freely in their own planes. Such a trial structure was postulated, therefore, with the molecules rotating about their centres of gravity, as in Fig. 1. Structure factors were then calculated, using the expression (given on p. 324 of the *International Tables for X-ray Crystallography*, Vol. 2, 1959) for atoms rotating about an axis. The assumed radii are given in Table 1. McWeeny's scattering-factor curve (1951) was used for the carbon atoms, but for convenience the nitrogen atom was assumed to be equivalent to 1·25 carbon atoms, this factor being chosen to give the best approximation to the nitrogen curve over the angular range considered. An isotropic temperature factor of 5·8 Å^2 was applied.

Table 1. *Details of proposed structure*

Atoms	Radius
1 N (≡ 1·25 C)	0·18 Å
1 C	1·51
1 C	2·46
2 C	1·30
2 C	2·18
2 C	2·19
2 C	2·32

The atoms are assumed to rotate about the origin, with the radii given above, in a plane containing the z-axis and inclined at 21½° to **a**.

The agreement with the observed structure amplitudes was reasonable, but the more intense reflections seemed to be affected by extinction. An empirical correction was therefore devised in the manner described by Pinnock, Taylor & Lipson (1956). The graph in Fig. 2 indicates that the strongest reflection is reduced by extinction to about a quarter of its real intensity.

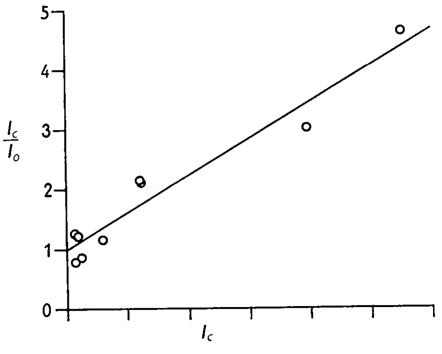


Fig. 2. Extinction correction.

A three-dimensional Fourier synthesis was computed, using the observed structure amplitudes (corrected for extinction) and the calculated phase angles. Two central sections of the average molecule are shown in Fig. 3. The synthesis indicates that the angle between the molecular plane and **a** is 21½°, rather than the 22½° originally assumed, and the structure factors were therefore recalculated for the revised value. The effect on the agreement was, however, very slight.

Observed and calculated data are compared in Table 2. Structure factors have been calculated not only for the 191 observed reflections, but also for the 247 unobserved but accessible reflections. For 231 of the latter group the calculated value is less than or equal to threshold; for the remaining 16 it is slightly greater. Of all the unobserved reflections only these 16 are included in Table 2. The agreement residual is 0·15, for observed reflections only. The detailed agreement is reasonable, and the approximate correctness of the proposed structure seems to be established.

Table 2. *Observed and calculated structure amplitudes, and calculated phase angles*

hkℓ	F_o	F_c	α
000	-	592	0
004	175	180	0
008	47	49	180
0,0,12	34	34	0
0,0,16	16	12	0
0,0,20	6	2	0
0,0,24	13	12	0
020	103	118	0
022	104	122	0
024	11	11	0
026	5	5	0
028	12	16	180
0,2,10	12	14	180
0,2,12	29	30	0
0,2,14	5	4	0
0,2,16	7	6	0
0,2,20	2	4	0
0,2,22	2	1	180
0,2,24	8	10	0
040	18	23	0
042	10	10	180
044	10	8	0
046	23	23	180
048	8	4	0
0,4,10	2	1	0
0,4,12	10	9	0
0,4,14	4	6	0
0,4,16	5	4	0
0,4,18	4	5	180
0,4,20	6	7	0
0,4,24	4	5	0
060	2	4	180
062	6	5	180
064	2	3	180
066	2	3	180
068	4	5	0
0,6,10	2	1	0
0,6,12	6	9	0
0,6,14	<2	3	180
0,6,16	4	4	0
0,6,20	2	1	0
0,6,22	2	2	0
080	4	3	0
084	3	4	0
088	2	4	0
112	189	179	0
116	44	35	180
1,1,10	16	8	0
1,1,14	28	26	0
1,1,22	8	9	0
1,1,26	6	7	0
121	93	85	166
123	68	57	189
125	24	23	189
127	10	9	82
129	6	10	320
1,2,11	7	5	20
1,2,13	6	2	99
130	60	55	0
132	50	38	0
134	7	9	0
136	10	5	0
138	16	18	180
1,3,10	18	18	0
1,3,12	3	3	0
1,3,14	10	10	0
1,3,18	3	2	0
1,3,20	3	3	180
1,3,22	6	9	0
1,3,24	4	1	0
1,3,26	3	4	0
141	36	36	182
143	24	23	180
145	5	5	161
147	7	7	333
149	6	8	25
1,4,11	3	3	322
1,4,13	3	1	173
1,4,15	3	2	149
150	14	10	0
152	14	14	0
154	4	1	0
156	4	2	0
1,5,10	4	5	0
1,5,12	3	3	0
1,5,14	5	6	0
1,5,16	3	4	180
1,5,18	4	5	0
1,5,22	3	4	0
1,5,24	3	2	0
161	3	3	208
163	3	2	80
165	3	4	334
167	4	5	23
169	3	3	324
172	6	5	0
174	2	3	180
176	4	5	0
178	<2	3	180
1,7,10	2	5	0
1,7,14	<2	3	0
181	2	2	23
183	2	2	337
185	2	2	27
220	43	40	0
224	4	3	0
228	7	4	0
2,2,12	24	22	0
2,2,16	5	3	0
2,2,20	4	6	0
2,2,24	6	9	0
231	34	34	154
233	12	22	226
235	14	14	76
237	15	14	329
239	9	9	4
2,3,11	3	4	69
2,3,13	3	5	229
2,3,15	3	3	161
2,3,19	4	3	310
240	38	40	0
242	26	24	0
244	24	21	0
248	8	6	0
2,4,12	7	6	0
2,4,16	5	4	0
2,4,20	6	7	0
2,4,24	3	4	0
251	16	18	194
253	11	10	157
255	2	3	277
257	4	6	18
259	4	4	5
2,5,13	3	4	133
2,5,15	<2	3	236
2,5,21	2	2	312
260	20	20	0
262	10	11	0
264	11	10	0
2,6,10	<2	3	180
2,6,12	3	5	0
2,6,16	3	4	0
271	5	6	163
273	3	3	207
280	4	4	0
332	12	10	0
336	7	2	0
3,3,10	10	8	0
3,3,14	7	6	0
3,3,18	5	5	0
3,3,22	4	7	0
341	<2	3	243
343	3	2	40
345	6	5	5
347	5	5	328
349	2	4	83
3,4,11	3	4	223
3,4,13	<2	3	183
3,4,15	3	2	96
3,4,17	3	3	306
3,4,19	<2	3	30
350	7	7	0
352	10	12	0
356	3	3	0
358	4	6	180
3,5,10	3	4	0
3,5,14	6	6	0
3,5,18	4	4	0
3,5,22	<2	3	0
361	9	10	189
363	4	6	163
365	3	2	243
367	2	3	60
369	<2	3	294
370	4	7	0
372	7	8	0
3,7,14	<2	3	0
381	4	5	166
383	3	3	203
390	2	3	0
392	2	3	0
394	1	1	0
396	1	1	0
440	3	6	180
444	2	4	180
448	3	4	0
4,4,12	8	8	0
4,4,16	6	5	0
4,4,20	2	4	0
455	3	2	357
460	5	6	0
462	<2	3	180
464	4	4	0
466	<2	3	180
468	3	3	0
4,6,12	3	4	0
480	5	4	0
482	3	3	0
484	3	2	0
4,8,12	<1	2	0
552	6	4	0
556	7	7	0
5,5,10	4	7	0
5,5,14	2	2	0
561	3	3	0
563	3	2	0
660	<2	3	0
664	<2	3	0

Nevertheless there are some significant discrepancies which suggest that the rather simple assumptions pertaining to molecular motion are not entirely adequate.

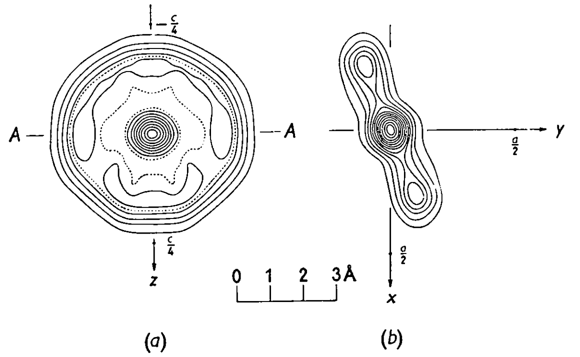


Fig. 3. Two sections of the Fourier synthesis. Solid contours are drawn at intervals of ½ e.Å^{-3}, the lowest being at ½ e.Å^{-3}. (*a*) Section in the plane of the molecule. A broken contour has been added at 2¼ e.Å^{-3} in order to emphasize the valley surrounding the central peak. The line *A–A* is the trace of the plane $z=0$. (*b*) Section at $z=0$.

The standard deviation of electron density has been estimated by the method of Cruickshank (Lipson & Cochran, 1953) to be about 0·15 e.Å^{-3}. (Only observed reflections were considered.) Some departures from the assumed radial symmetry of the molecule are apparent in Fig. 3(*a*); the greatest difference in electron density for points equidistant from the centre is about 0·5 e.Å^{-3}. Such differences may signify a small degree of hindrance to molecular rotation, but no unique inference can be drawn from such evidence, and further refinement of the structure does not seem to be practicable.

Discussion

An oblique view of the region of one unit cell is given in Fig. 4. The scattering units are shown as discs, and on these are superimposed conventional molecules in random orientations to represent the structure as it might appear at a given instant. The shortest possible intermolecular distances in the proposed structure are 3·26 Å (for molecules related by the *a* glide) and 3·22 Å (for molecules related by the screw tetrad). In the assumed structure these rather small distances would occur relatively infrequently; in the actual structure they probably do not occur at all. Any tendency to crowding by reason of rotation would be met by compensating translational vibrations, and by coupling of the motions of adjacent molecules. For example, two molecules related by the screw tetrad, and thus in edge contact, might be expected to mesh, like gears. The system is visualized as one of loosely-coupled rotations and vibrations, with probably a small degree of hindrance, and this mechanism may well be the origin of the strong diffuse scattering mentioned earlier.

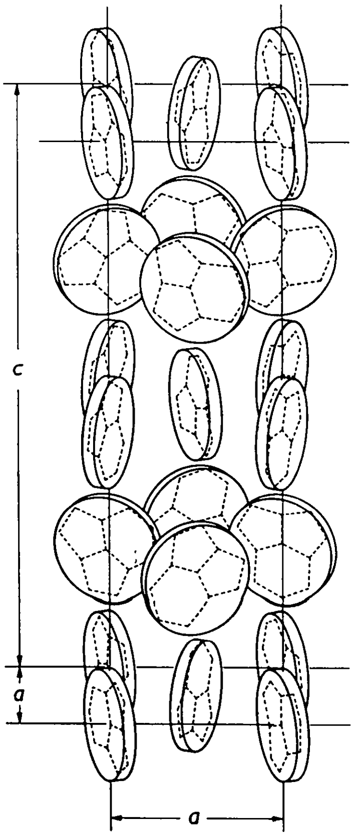


Fig. 4. An oblique view of the region of one unit cell.

In this discussion it has been assumed that molecular rotation actually occurs. This is almost certainly true just below the melting point, but it is possible that at room temperature the molecules are stopped in nearly-random orientations. The two possibilities cannot be distinguished on the basis of X-ray evidence alone.

The apparent molecular rotation in the tetragonal phase is a barrier to investigation of the molecular structure. What of the monoclinic phase? It might be thought that the phase transition corresponds to a cessation of rotation (or to an ordered reorientation) of the molecules, but examination of the three-dimensional intensity data indicates that this can hardly be so. The intensities decrease with Bragg angle just as rapidly as those for the tetragonal phase. In order to illustrate this point, the apparent temperature factors were estimated by Wilson's statistical method (1942). The value obtained for the monoclinic phase was 9·5 Å^2, and for the tetragonal phase (after the observed data had been corrected for extinction) it was 9·8 Å^2. It can only be concluded that apparent molecular rotation occurs in this phase also.

The considerations of the preceding paragraph suggest that an anomalously high apparent temperature factor (as indicated by Wilson's method) may provide early warning of rotation or random orientation of the molecules.

Some of the computations for this project were carried out by Dr F. R. Ahmed of this laboratory, using facilities generously made available by the Commanding Officer and staff of No. 1 Army Pay Ledger Unit (IBM 650), and the staff of the Structures Laboratory, National Aeronautical Establishment (TRANSFER, formerly FERUT). The sample of cycl(3,2,2)azine was provided by Prof. Boekelheide. It is a pleasure to record my indebtedness to these people, and to Dr W. H. Barnes of this laboratory for advice and encouragement.

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