

supplementary criterion of the similarity of these crystal structures. The ratio for PHI is 0.496, which is different from those of the other three in Table 6.

The mutual similarity of the sheet structures can be specified by the circularity of the hexagon formed by the six neighbours. The circularity may be defined by

$$\left(x - \frac{b}{2}\right) / \left(\frac{b}{2}\right),$$

where b is the b -translation distance and x is the distance between the centres of dimeric units related by the twofold screw axis.

The circularity of ISA is closer to that of IST than to that of CSA. The circularity and ϵ_2 indicate that ISA with a six-membered heterocyclic ring is isomorphous with IST with a five-membered one.

In ISA, IST and CSA, any molecule in the sheet has one neighbouring dimer which links the molecule at both ends through C—H...O interactions (Fig. 4). This may be a requisite for the formation of the sheet structures in these compounds. In PHI such interactions exist only in the $[0\bar{1}1]$ direction because of the geometric restriction of the dimeric unit, thus resulting in a ribbon instead of a sheet.

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Temperature-Dependent Hindered Rotation in the 1:1 Complex of Cycl[3.2.2]azine and *s*-Trinitrobenzene*

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At 293 K crystals of the complex ($C_{10}H_7N \cdot C_6H_3N_3O_6$; FW 354.3) are monoclinic, $P2_1/n$, $a = 14.37$ (1), $b = 15.99$ (1), $c = 6.682$ (4) Å, $\beta = 92.17$ (5)°, $D_m = 1.532$, $D_x = 1.533$ g cm⁻³, $Z = 4$. On cooling, an abrupt, reversible phase change occurs at 143 ± 3 K, with a doubling of the volume of the unit cell, and of the asymmetric unit. Below the transition temperature the crystals are monoclinic $P2_1/c$ with, at 91 K, $a = 15.528$ (8), $b = 15.636$ (8), $c = 13.102$ (6) Å, $\beta = 113.56$ (5)°, $Z = 8$. The structure at 293 K was refined by Fourier and least-squares methods (1580 independent reflexions) to a final R index of 0.18. It consists of stacks of alternating cycl[3.2.2]azine and *s*-trinitrobenzene molecules with a mean separation of 3.34 Å. The cycl[3.2.2]azine molecule appears to undergo hindered rotation in its own plane, with three preferred orientations. The structure at 91 K was refined by least-squares methods (4610 independent reflexions) to a final R index of 0.050. It is similar to the structure at 293 K, but the stack element comprises two differently-oriented molecules of each type with a mean separation of 3.27 Å. One of the cycl[3.2.2]azine molecules appears to be completely ordered, but for the other an alternative orientation is found for about 5% of the sites.

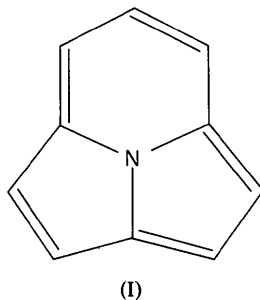
* Issued as NRCC No. 16654.

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Introduction

The X-ray analysis of cycl[3.2.2]azine (I) (Windgassen, Saunders & Boekelheide, 1959) was undertaken many years ago, for the purpose of establishing the precise molecular geometry. The analysis failed, however, because the X-ray data were found to be consistent with free rotation of the molecule in its own plane (Hanson, 1961*a*). Subsequent analysis of a dibromo derivative was of limited accuracy because of difficulties with the specimen, as well as the disproportionately large scattering power of the Br atoms (Hanson, 1961*b*). An analysis of the 1:1 complex of the material with *s*-trinitrobenzene was then undertaken. It was decided to conduct the study at a low temperature, and it was then discovered that, on cooling, a reversible phase change occurred. In view of the potential interest of this phenomenon, it was decided to study the structure at room temperature also. The room- and low-temperature forms are arbitrarily designated as *A* and *B* respectively.



Experimental details

The complex was crystallized from a toluene solution of approximately stoichiometric proportions of the components. The crystals were orange six-sided needles with faces {100} and {110}. These were easily cleaved normal to the needle axis (*c*) to give approximately equidimensional specimens. Crystal class and space group were determined from precession photographs, and unit-cell constants by diffractometric measurement of high-angle reflexions. Crystal data for two temperatures are given above. However, in order to facilitate comparison of the two forms, it is convenient to describe the structure of the *B* form in terms of a non-standard centred cell: $B2_1/d$, $a = 28.474$, $b = 15.636$, $c = 13.102$ Å, $\beta = 91.39^\circ$ (91 K), $Z = 16$. Thus the phase change corresponds to a doubling of the *a* and *c* cell edges. There is, moreover, an obvious correspondence between the intensities of reflexions $2h, k, 2l$ of the *B* form, and hkl of the *A* form.

The specimen used for intensity measurement at room temperature (293 K) was of maximum dimension

0.2 mm. The intensities of 2609 independent reflexions within the limiting sphere $2\theta = 130^\circ$ were measured with a Picker four-circle automatic diffractometer, using Ni-filtered Cu $K\alpha$ radiation, and a scintillation counter. The θ - 2θ scan method was used, with scans of 2° for $2\theta < 100^\circ$, and 3° otherwise. Background counts were taken from an experimentally-determined function of θ . 1029 reflexions were treated as unobserved, as their net intensities were less than either 30 counts, or 20% of the corresponding background intensity. The specimen used for intensity measurement at 91 K was of maximum dimension 0.25 mm. It was protected from thermal shock by being enclosed in (but not touching) a thin-walled fused-quartz capillary. Intensity measurements were essentially as described above except that the diffractometer was manually set (General Electric XRD5), and had a limiting sphere $2\theta = 165^\circ$. It was found that many reflexions had to be centred by small perturbations to the precomputed goniostat settings, perhaps because of steep and varying thermal gradients in the goniometer head and goniostat. Thus very weak reflexions could not be measured with confidence, and were not scanned. Such reflexions were treated as unobserved, and their net intensities assumed to be less than 10% of the corresponding background intensity. Of the 6607 accessible reflexions, significant intensity was recorded for 4610. No absorption corrections were applied to either data set ($\mu = 11.0$ cm $^{-1}$, 91 K).

The various temperatures used in the measurements summarized in Fig. 1 were controlled by means of a 'cryo-collimator' (Materials Research Corporation). Specimen temperature was estimated ultimately by substitution of a thermocouple for the specimen, with conditions otherwise unchanged. The thermocouple was itself calibrated by contact with liquid nitrogen (77 K), solid CO $_2$ (194.5 K) and solid H $_2$ O (273 K). The Bragg angle of the intense reflexion designated 008 for the *A* form, and 0,0,16 for the *B* form, was used to evaluate $c \sin \beta$ (Fig. 1) and provided a sensitive secondary standard of specimen temperature. The fixed temperature of 91 K, used for intensity data collection for the *B* form, was maintained with a cryostat of local construction. This used the same principle as the 'cryo-collimator' (cold nitrogen stream, with surrounding curtain of dry, room-temperature nitrogen), but was much more economical in consumption of liquid nitrogen.

The phase transition

Fig. 1 summarizes the temperature dependence of the cell constants and of the intensities of specific reflexions. It will be noted that the two branches of the first curve overlap for a range of 6 K. The overlap results from the fact that on cooling the transition was

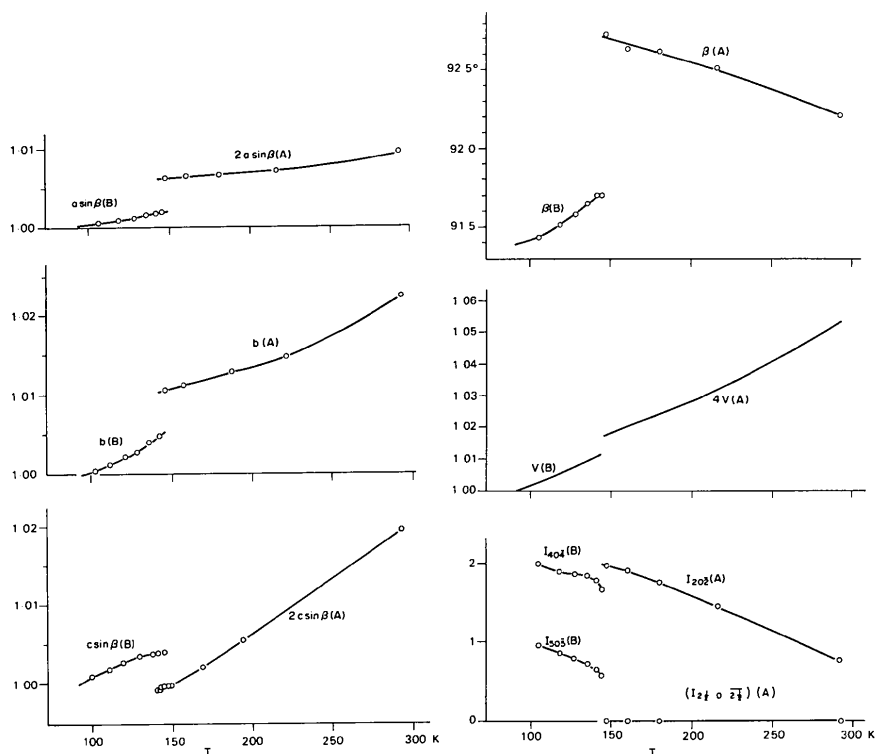


Fig. 1. Variation of some crystal properties with temperature. Length and volume are expressed as a fraction of the corresponding value at 91 K. The scale of intensities is arbitrary.

observed to occur as low as 140 K, while on warming the reverse transition might not occur below 146 K. However, the transition was found to be abrupt and complete at whatever temperature it occurred. The volume of the unit cell is not conserved during the transition.

Structure determination

The structure at 293 K was determined by symbolic addition procedures, with the usual difficulties associated with planar molecules having hexagonally-symmetric elements. Refinement of a plausible trial structure was discouragingly slow, and was terminated when, at $R = 0.18$, the apparent bond lengths and thermal parameters of the cycl[3.2.2]azine molecule had become unrealistic. (Block-diagonal least-squares refinement was used, minimizing $\sum w\Delta F^2$, where $w = F_o^2/400$ for $F_o < 20$, $= 400/F_o^2$ otherwise. Unobserved reflexions were not included in the refinement.) Examination of the F_o synthesis suggested a disorder structure in which the cycl[3.2.2]azine molecule can assume various orientations in a plane while occupying essentially the same space. It was concluded that the

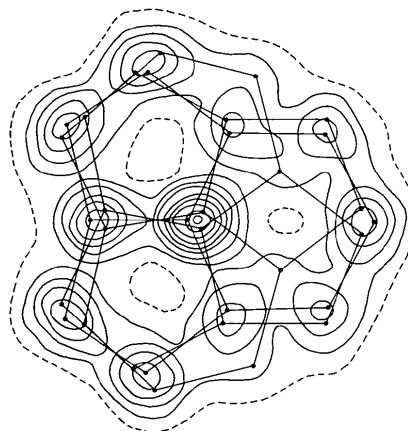


Fig. 2. Electron density of the *A* form in the plane of the cycl[3.2.2]azine molecule. The contours are at intervals of $1 \text{ e } \text{Å}^{-3}$; the lowest contour, at $1 \text{ e } \text{Å}^{-3}$, is broken. The three inferred molecular orientations are indicated.

structure as perceived at this point was approximately correct, and the information available was used to assist in the analysis of the *B* form, to be described below. On completion of this analysis, the deduced geometry of the cycl[3.2.2]azine molecule was used in a

plausible model in which it was assumed that the molecule adopted, with equal frequency, the three orientations shown in Fig. 2. The R index for this model is 0.18. While this value is high, it is probably not unduly so for a disorder structure which cannot be properly refined. The agreement is worst for the very weak reflexions, which constitute a large fraction of the data set. If the reflexions whose amplitudes are less than twice the nominal threshold value of 4.0 are excluded, $R = 0.11$ for the remaining 700. The difference electron density in the plane of the molecule suggests that the model could be improved by the inclusion of still more orientations. The ultimate model would presumably include a probability function of position and orientation. However, no attempt has been made to improve the crude model already described.

The structure of the B form was solved by assuming it to be sufficiently similar to the A form that corresponding reflexions have the same sign. That is, the sign of $2h, k, 2l$ of the B form should have the sign of hkl of the A form. Obviously no prediction can be made for the reflexions with h (and l) odd, and therefore a Fourier synthesis of reflexions signed in this way must represent a superposition of structures related by the translation $a/2$ (or $c/2$). Such a synthesis was found to be consistent with a single orientation for the *s*-trinitrobenzene molecule, and two orientations, differing by 134° , for the cycl[3.2.2]azine molecule. An appropriate trial structure was readily refined by Fourier methods and by block-diagonal least squares. The weighting scheme, chosen to minimize dependence of the weighted residual on F_o and θ , was $w = w_1 w_2$, where $w_1 = 40/F_o$ for $F_o < 40$, $= 80/(40 + F_o)$ otherwise, and $w_2 = \sin \theta / 0.633$ for $\sin \theta < 0.633$, $= 1$ otherwise.

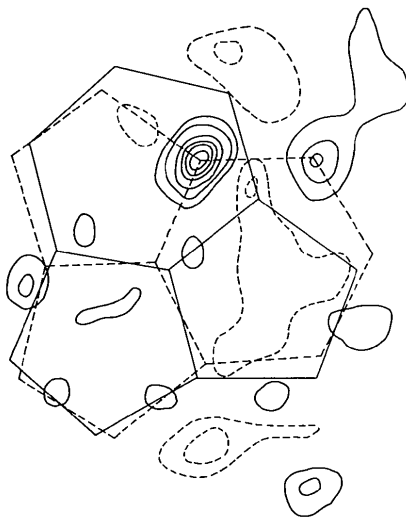


Fig. 3. Difference electron density of the B form in the plane of the cycl[3.2.2]azine molecule $C(2)$. The contours are at intervals of $0.1 \text{ e } \text{\AA}^{-3}$, the zero contour is omitted, and negative contours are broken. The solid molecular outline indicates the predominant orientation, and the broken outline the proposed alternative orientation.

(Unobserved reflexions were not included in the refinement.) A correction for extinction was calculated as described by Pinnock, Taylor & Lipson (1965). It was judged to be inappropriate for the two strongest reflexions, which were omitted from the analysis, but was applied to the next 33 most intense reflexions, the largest correction being 19% of F_o . Three weak reflexions for which the calculated amplitudes were persistently below threshold were arbitrarily assigned zero weight. The refinement converged at $R_w = 0.0544$ ($R = 0.0513$, for observed reflexions only). At this stage examination of the difference electron density revealed two extraneous peaks in the plane of one of the cycl[3.2.2]azine molecules. These were interpreted as illustrated in Fig. 3: an alternative orientation is adopted by $5 (\pm 2)\%$ of the molecules at the site. (The occupancy was evaluated by comparing the electron densities of the extraneous peaks with that of a typical C atom; the estimate of precision acknowledges the difference in height of these ideally equal peaks.) Appropriate contributions were included in the structure factors, on the assumption of the best available molecular geometry, and reasonable thermal motion. Refinement of the other parameters was continued, with ultimate convergence at $R_w = 0.0527$, $R = 0.0496$. The resulting ratio of residuals (\mathcal{R}) is 1.03, indicative of a significant improvement (Hamilton, 1965). The contribution of the molecule in the alternative orientation can be specified by only four parameters, and for this problem $n-m > 4000$. From *International Tables for X-ray Crystallography* (1974), $\mathcal{R}_{4,4000,0.005} = 1.0019$.

In the ultimate refinement cycle no coordinate shift of a non-hydrogen atom exceeded 0.001 \AA , or 40% of the corresponding e.s.d. Final coordinates for the structures of the A and B forms are given in Table 1.*

The accuracy of the analysis of the A form is such that any consideration of molecular geometry is pointless. For the B form, the nominal e.s.d. of bond distances ranges from 0.0025 to 0.0039 \AA . The reliability of e.s.d.'s can be checked by the agreement among relatively large groups of chemically equivalent bonds. There are, for example, twelve independent measures of the C—C distance in *s*-trinitrobenzene. The formal standard deviation of these is 0.004 \AA , compared with a mean *estimated* value of 0.003 \AA . It would seem prudent, therefore, to increase all e.s.d.'s by 30%. If this is done, the greatest range of values for any group of chemically equivalent bond lengths is scarcely significant ($\Delta l = 0.017 \text{ \AA}$, $t = 3.0$).

* Lists of structure factors, thermal parameters (anisotropic for C, N and O), bond lengths and angles and details of some molecular planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33410 (48 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final atomic coordinates with e.s.d.'s where applicable ($\times 10^3$ for H atoms, $\times 10^4$ otherwise)*General positions: *A* form: $\pm(x,y,z)$; $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; *B* form: $(0,0,0; \frac{1}{2}, 0, \frac{1}{2}) \pm (x,y,z)$; $\frac{1}{4} + x, \frac{1}{4} - y, \frac{1}{4} + z$.

A FORM			x			y			z					
<i>s</i> -Trinitrobenzene									Cycl[3,2,2]azine, third orientation			First cycl[3,2,2]azine C(1)		
C(1)	8289(7)	6362(8)	1145(15)	N(216)	2482	9298	1216	N(16)	1248(1)	9421(1)	591(1)			
C(2)	8456(8)	5515(7)	1244(15)	C(217)	2643	8453	1141	C(17)	1609(1)	9998(1)	623(2)			
C(3)	7679(8)	5021(8)	1256(15)	C(218)	3581	8236	1167	C(18)	2056(1)	9629(2)	650(2)			
C(4)	6785(7)	5346(7)	1149(14)	C(219)	4254	8872	1263	C(19)	2093(1)	8732(2)	648(2)			
C(5)	6679(7)	6168(8)	1062(13)	C(220)	4025	9724	1335	C(20)	1701(1)	8191(1)	612(2)			
C(6)	7436(8)	6710(7)	1056(15)	C(221)	3092	9958	1311	C(21)	1254(1)	8542(1)	577(2)			
N(7)	9142(7)	6924(7)	1140(14)	C(222)	2501	10680	1352	C(22)	764(1)	8317(2)	540(2)			
N(8)	7832(8)	4074(7)	1390(13)	C(223)	1583	10410	1279	C(23)	501(1)	9065(2)	546(2)			
N(9)	5729(7)	6544(7)	952(14)	C(224)	1569	9518	1191	C(24)	812(1)	9776(2)	578(2)			
O(10)	8969(6)	7654(6)	850(14)	C(225)	1085	8740	1090	C(25)	900(1)	10676(2)	593(2)			
O(11)	9884(5)	6603(7)	1442(13)	C(226)	1729	8093	1060	C(26)	1383(1)	10812(1)	623(2)			
O(12)	8608(8)	3856(6)	1464(16)	Occupancy 0.33										
O(13)	7121(8)	3697(6)	1331(14)	B FORM										
O(14)	5102(5)	6058(7)	1054(14)	First <i>s</i> -trinitrobenzene T(1)										
O(15)	5678(7)	7305(6)	784(16)	C(1)	4129(1)	6437(1)	540(2)	H(18)	232(1)	997(2)	64(2)			
H(2)	912	525	138	C(2)	4268(1)	5584(1)	585(2)	H(19)	240(1)	846(2)	68(2)			
H(4)	619	495	112	C(3)	3913(1)	4982(1)	613(2)	H(20)	174(1)	759(2)	61(2)			
H(6)	732	735	92	C(4)	3441(1)	5190(1)	599(2)	H(21)	64(1)	775(2)	52(3)			
				C(5)	3329(1)	6054(1)	558(2)	H(22)	15(1)	911(2)	57(2)			
				C(6)	3664(1)	6691(1)	524(2)	H(25)	67(1)	1112(2)	57(2)			
				N(7)	4499(1)	7091(1)	509(1)	H(26)	155(1)	1135(2)	64(2)			
				N(8)	4041(1)	6073(1)	639(1)	Second cycl[3,2,2]azine C(2)						
				N(9)	2829(1)	6298(1)	548(1)	Predominant orientation, occupancy 0.95						
				O(10)	4390(1)	7799(1)	198(1)	N(116)	6348(1)	9317(1)	590(1)			
				O(11)	4896(1)	6884(1)	796(1)	C(117)	6039(1)	10001(2)	627(2)			
				O(12)	4460(1)	3897(1)	650(1)	C(118)	5569(1)	9762(2)	611(2)			
				O(13)	3721(1)	3545(1)	652(1)	C(119)	5460(1)	8882(2)	548(2)			
				O(14)	2540(1)	5724(1)	626(1)	C(120)	5796(1)	8226(2)	505(2)			
				O(15)	2734(1)	7053(1)	457(2)	C(121)	6269(1)	8448(2)	527(2)			
				H(2)	460(1)	546(2)	59(2)	C(122)	6732(1)	8091(2)	517(2)			
				H(4)	319(1)	475(2)	61(2)	C(123)	7054(1)	8758(2)	582(2)			
				H(6)	357(1)	728(2)	52(2)	C(124)	6804(1)	9544(2)	624(2)			
				Second <i>s</i> -trinitrobenzene T(2)										
				C(101)	9193(1)	6253(1)	603(2)	H(118)	532(1)	1020(2)	692(2)			
				C(102)	9226(1)	5365(1)	634(2)	H(119)	514(1)	874(2)	57(2)			
				C(103)	8808(1)	4910(1)	605(2)	H(120)	571(1)	765(2)	48(2)			
				C(104)	8370(1)	5296(1)	531(2)	H(122)	681(1)	750(2)	47(2)			
				C(105)	8365(1)	6184(1)	509(2)	H(123)	741(1)	872(2)	60(2)			
				C(106)	8768(1)	6677(1)	543(2)	H(125)	705(1)	1082(2)	72(2)			
				N(107)	9629(1)	6760(1)	626(1)	H(126)	622(1)	1135(2)	73(2)			
				N(108)	8833(1)	3974(1)	661(1)	Second cycl[3,2,2]azine C(2)						
				N(109)	7907(1)	6619(1)	431(1)	Alternative orientation, occupancy 0.05						
				O(110)	9594(1)	7535(1)	529(1)	N(216)	6300	9196	585			
				O(111)	10002(1)	6374(1)	742(1)	C(217)	6732	9589	624			
				O(112)	9221(1)	3643(1)	791(1)	C(218)	6710	10475	685			
				O(113)	8462(1)	3583(1)	579(1)	C(219)	6272	10879	702			
				O(114)	7551(1)	6179(1)	472(1)	C(220)	5845	10427	660			
				O(115)	7908(1)	7395(1)	328(1)	C(221)	5857	9534	598			
				H(102)	953(1)	508(2)	66(2)	C(222)	5553	8607	539			
				H(194)	808(1)	500(2)	52(2)	C(223)	5831	8077	495			
				H(106)	874(1)	727(2)	57(2)	C(224)	6314	8327	525			
								C(225)	6801	8129	524			
								C(226)	7057	8887	583			

The thermal motion of the cycl[3.2.2]azine molecules has been analysed in terms of rigid-body modes by the method of Schomaker & Trueblood (1968). The principal mode for each is libration about an axis normal to the molecular plane, passing within the carbon perimeter. The r.m.s. amplitudes (2.7 and 2.0° respectively) are too small for the librations to affect the bond lengths appreciably, and corrections have not been applied.

The scattering factors were taken from Stewart, Davidson & Simpson (1965) for H, and from Hanson, Herman, Lea & Skillman (1964). The computer programs used were those of Gantzel & Trueblood (MGTLS, thermal-motion analysis), and of Ahmed, Hall, Pippy & Huber (1966).

Discussion

The primary result of the analysis is soon stated: cycl[3.2.2]azine is essentially planar, with bond lengths and angles as given in Fig. 4. (The *s*-trinitrobenzene molecules have typical geometry, with the NO₂ groups bent and twisted out of the molecular plane by as much as 22°.) However, in view of the unusual phase transition, it seems appropriate to describe and compare the structures of the *A* and *B* forms.

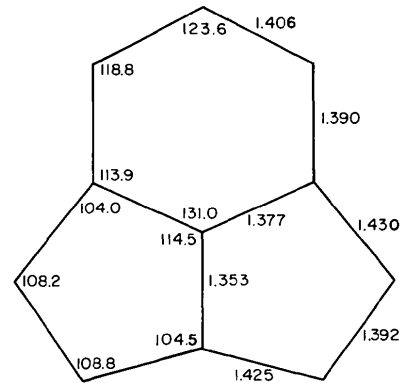


Fig. 4. Mean bond lengths (Å) and angles (°) for cycl[3.2.2]azine. E.s.d.'s are 0.004 Å and 0.3°.

The *A* form consists of stacks, parallel to *c*, of alternating cycl[3.2.2]azine and *s*-trinitrobenzene molecules. These are within 3° of being normal to *c*, and are separated by 3.34 Å. Each cycl[3.2.2]azine molecule is thus constrained to lie in a specific plane, but otherwise its closest intermolecular contacts involve its H atoms and the O atoms of the *s*-trinitrobenzene molecules of neighbouring stacks. These contacts do not obviously fix the orientation of the molecule in its

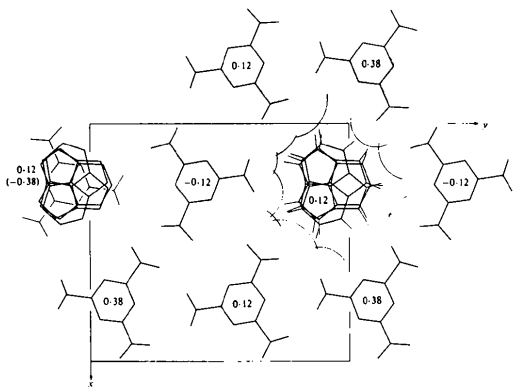


Fig. 5. Part of the structure of the *A* form, viewed along *c*. The numbers are the approximate *z* coordinates of the several molecules. An additional *s*-trinitrobenzene molecule (at *z* = -0.38) has been included to illustrate the overlap. The arcs define a contact envelope for the cycl[3.2.2]azine molecule, as described in the text.

plane. The arcs shown in Fig. 5 define an envelope within which all points in the molecular plane are more than 2.4 Å (a nominal sum of van der Waals radii of O and H) from any O atom. Thus it can be seen that all three assumed orientations of the cycl[3.2.2]azine molecule are sterically acceptable. It can also be shown (and may perhaps be apparent from Fig. 5) that *all* orientations of the molecule are acceptable, provided that small in-plane translations are permitted. Thus there seems to be no steric reason why the molecule should not rotate in its own plane.

The structure of the *B* form is similar, except that the stack unit comprises two molecules of each type. (The normals to the molecular planes are inclined at from 0.6 to 3.5° to *c*.) The two *s*-trinitrobenzene molecules differ in orientation by 12°, and the contact envelopes defined by the O atoms do not permit rotation of the cycl[3.2.2]azine molecules (Fig. 6). For each envelope there are but two possible orientations (or, more precisely, two narrow ranges of orientation). These possibilities are used in varying degrees. Thus only one orientation is found for the envelope of *C*(1); the other (indicated by a dotted outline) does not occur to any detectable degree. For the other envelope one orientation occurs for 95% of the molecules, and the other (indicated by a dashed outline) for 5%. Comparison of Figs. 5 and 6 demonstrates that all of the orientations inferred for the *A* form are represented in the *B* form, albeit in unequal ratio. The principal modes of molecular overlap are illustrated in Fig. 6. Little can be said of these, except that the centres of gravity of the two molecules tend to lie one above the other.

During the transition from *B* to *A* (that is, with increasing temperature) the *s*-trinitrobenzene molecules change their orientations slightly, and become indistinguishable. At the same time, constraints on the orientation of the cycl[3.2.2]azine molecules are relaxed, and these molecules rotate, at random, some through angles as great as 134°. The result is a disorder structure as

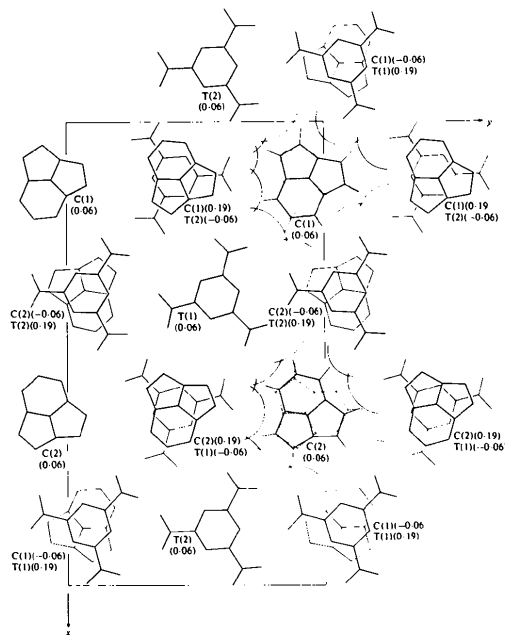


Fig. 6. Part of the *B* structure, viewed along *c*. The molecule types and numbers (Table 1) and approximate *z* coordinates are given. The arcs define contact envelopes as in Fig. 5. The dotted (very faint) outline indicates a possible but unused orientation for *C*(1), while the broken outline indicates the proposed alternative orientation for *C*(2).

described. It seems unreasonable to suppose that such rotation could occur only at the transition temperature, and not at, for example, room temperature, particularly since, as we have seen, rotation at this temperature is sterically possible. For this reason it is suggested that the condition of the *A* form should be described as hindered rotation.

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