The Crystal and Molecular Structures of 2*H*-1,3-Benzoxazine-2,4(3*H*)-dione (CSA) and 2*H*-3,1-Benzoxazine-2,4(1*H*)-dione (ISA)

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The crystal structures of CSA and ISA have been determined from visually estimated Cu $K\alpha$ data. The unit-cell data are: $P2_1/a$, $a = 8\cdot41$ (1), $b = 15\cdot87$ (1), $c = 5\cdot27$ (1) Å, $\beta = 90\cdot5$ (2)°, $Z = 4$ for CSA; and $P2_1/a$, $a = 7\cdot18$ (2), $b = 14\cdot35$ (2), $c = 6\cdot73$ (1) Å, $\beta = 91\cdot9$ (3)°, $Z = 4$ for ISA. The structures were refined by block-diagonal least-squares calculations to R values of $0\cdot058$ and $0\cdot095$ for 999 and 1121 non-zero reflexions for CSA and ISA respectively. The angles C–N–C [127·3 (2)° for CSA, 124·1 (3)° for ISA] and lengths of the exocyclic C–O [1·219 (3) Å for CSA, 1·213 (4) Å for ISA] indicate that the ketonic form is the preferred tautomer in the crystals. In both crystals, the molecules related by a centre of symmetry are linked together by a C=O···H–N hydrogen bond to form a dimer. The dimers related by twofold screw axes are held together by C–H···O interactions (H···O 2·39 and 2·48 Å for CSA, 2·58 and 2·61 Å for ISA) to form a sheet. The sheets are packed along **c**, so that the molecules related by an *a* glide plane overlap nearly parallel. The crystals of ISA are isomorphous with those of isatin.

Introduction

The importance of a precise knowledge of the critical conditions of isomorphous replacement in organic crystals is obvious from the viewpoint of the systematization of organic crystal chemistry. Kitaigorodsky (1961) has proposed a concept of the degree of molecular isomorphism, on the basis of his theory of close packing of molecules, to determine the conditions of morphotropism, but there are many unsolved problems concerning the scope of its applicability. The present investigation was undertaken to examine the determining factors of crystal morphotropism in the two isomers of dihydrobenzoxazine-dione (CSA and ISA), which belong to the same space group and have similar cell dimensions, and to extend the scope of our programme of study on molecular packing of conjugated heterocyclic compounds (Kashino & Haisa, 1973; Shimizu, Kashino & Haisa, 1975).

Experimental

Crystals of CSA and ISA were grown from ethanol solutions by slow evaporation as colourless plates developed on (010). Intensities were estimated visually on equi-inclination Weissenberg photographs and were corrected for Lorentz and polarization factors and for spot shape. Crystal data and experimental details are summarized in Table 1.

Structure determination and refinement

The structures of CSA and ISA were solved by the symbolic addition procedure and by the Patterson method respectively, and refined by block-diagonal least-squares calculations. At the later stages, the

Table 1. *Crystal data and experimental details*

	CSA	ISA
	$C_8H_5NO_3$	$C_8H_5NO_3$
m.p. (°C)	244–248 in a sealed glass capillary (sublimes)	243–245 (dec.)
Systematic absences	$h0l$, h odd $0k0$, k odd	$h0l$, h odd $0k0$, k odd
Space group	$P2_1/a$	$P2_1/a$
a (Å)	8·41 (1)*	7·18 (2)
b (Å)	15·87 (1)	14·35 (2)
c (Å)	5·27 (1)	6·73 (1)
β (°)	90·5 (2)	91·9 (3)
V (Å³)	703 (1)	693 (3)
Z	4	4
D_x (g cm⁻³)	1·541	1·564
D_m (g cm⁻³)	1·54	1·55
Flotation mixture	KI–H₂O	Xylene–CCl₄
μ(cm⁻¹) for Cu $K\alpha$	10·4	10·5
Dimensions of specimens used (mm)	0·25 × 0·18 × 0·60	0·40 × 0·12 × 0·18 0·45 × 0·15 × 0·20
Layers photographed	$hk0$ to $hk4$	$hk0$ to $hk5$ $0kl$ to $5kl$
Non-zero reflexions	999	1121

* The cell constants and density for CSA reported by Scholl & Carson (1963) are incorrect.

Table 2. *The final positional parameters* ($\times 10^4$) *of the non-hydrogen atoms with standard deviations in parentheses*

	x	y	z
(a) CSA			
O(1)	3180 (2)	3172 (1)	4868 (3)
O(2)	2693 (2)	4501 (1)	5775 (4)
O(3)	5746 (2)	3995 (1)	−1107 (4)
N	4215 (2)	4239 (1)	2330 (4)
C(1)	3325 (3)	4009 (1)	4404 (5)
C(2)	4999 (3)	3711 (1)	671 (5)
C(3)	5507 (3)	2197 (1)	−250 (5)
C(4)	5265 (3)	1358 (1)	330 (5)
C(5)	4340 (3)	1138 (1)	2404 (6)
C(6)	3638 (3)	1742 (1)	3917 (5)
C(7)	3888 (3)	2581 (1)	3306 (5)
C(8)	4805 (3)	2815 (1)	1242 (4)
(b) ISA			
O(1)	3136 (3)	4356 (2)	598 (3)
O(2)	3890 (4)	5429 (2)	2826 (4)
O(3)	2361 (4)	3351 (2)	−1746 (4)
N	4231 (4)	3909 (2)	3689 (4)
C(1)	3784 (4)	4606 (2)	2431 (5)
C(2)	2944 (4)	3439 (2)	−84 (5)
C(3)	3296 (5)	1763 (2)	826 (6)
C(4)	3781 (5)	1092 (2)	2236 (7)
C(5)	4437 (5)	1360 (2)	4098 (6)
C(6)	4596 (5)	2295 (2)	4613 (5)
C(7)	4099 (4)	2967 (2)	3203 (5)
C(8)	3460 (4)	2711 (2)	1332 (5)

HBLS-5 and DAPH (Ashida, 1973). The final atomic parameters are listed in Tables 2 and 3.*

Results and discussion

Molecular structures

For both compounds the displacements of atoms from the least-squares planes of the benzene rings and the hetero-rings are listed in Table 4. The molecules are substantially planar. Bond lengths and angles are shown in Fig. 1. The C—C lengths in the benzene rings are normal, but the inner angles at C(3) and C(6) are slightly smaller than the sp^2 angle.

The values of bond lengths in the hetero-rings are in fair agreement with those from the simple HMO calculation, as shown in Table 5. However, in ISA C(1)—N is somewhat shorter and C(2)—O(1) is longer than the calculated values. The planarity of the hetero-rings indicates that the O and N atoms in the rings have

refinements were carried out using the weighting scheme: $w = 1 \cdot 0$ for $0 < |F_o| \leq F_{max}$, $w = (F_{max}/|F_o|)^2$ for $|F_o| > F_{max}$, F_{max} being 6·0 for CSA, and 5·0 for ISA. The final R values were 0·058 and 0·095 for 999 and 1121 non-zero reflexions for CSA and ISA respectively.

Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The computations were carried out on an NEAC 2200-500 computer at the Okayama University Computer Center. The programs used were *SIGM*, *TANG*,

Table 3. *The final parameters* ($\times 10^3$, *except B*) *of the hydrogen atoms*

	x	y	z	B (Å²)
(a) CSA				
H(1)	429 (3)	479 (2)	196 (6)	4·0 (8)
H(2)	613 (3)	235 (2)	−171 (5)	2·4 (5)
H(3)	586 (3)	95 (2)	−81 (5)	2·8 (6)
H(4)	425 (4)	51 (2)	289 (6)	4·8 (8)
H(5)	301 (4)	164 (2)	538 (6)	4·2 (7)
(b) ISA				
H(1)	473 (5)	407 (2)	479 (5)	0·7 (7)
H(2)	279 (6)	155 (3)	−37 (7)	2·6 (10)
H(3)	368 (7)	50 (4)	191 (8)	3·8 (12)
H(4)	483 (6)	88 (3)	515 (6)	2·3 (9)
H(5)	502 (6)	256 (3)	594 (6)	2·1 (8)

Table 4. *The least-squares planes and displacements (Å) of the atoms from the planes*
$$(X = ax + cz \cos \beta, \ Y = by, \ Z = cz \sin \beta)$$

Plane I: benzene ring
CSA: $-0·8083X − 0·0139Y − 0·5886Z + 3·7121 = 0$
ISA : $-0·9478X − 0·0055Y + 0·3187Z + 2·0604 = 0$

	CSA	ISA		CSA	ISA
C(3)*	−0·0031	−0·0021	N	0·0390	0·0194
C(4)*	0·0019	0·0053	C(1)	0·0131	0·0214
C(5)*	−0·0003	−0·0048	C(2)	0·0264	0·0102
C(6)*	−0·0000	0·0010	H(1)	0·091	−0·061
C(7)*	−0·0012	0·0021	H(2)	0·013	0·061
C(8)*	0·0028	−0·0016	H(3)	−0·047	0·006
O(1)	−0·0113	0·0330	H(4)	−0·070	−0·021
O(2)	0·0125	0·0362	H(5)	−0·020	0·025
O(3)	0·0573	0·0159			

Plane II: hetero-ring
CSA: $-0·8132X − 0·0280Y − 0·5814Z + 3·7829 = 0$
ISA: $-0·9472X − 0·0166Y + 0·3201Z + 2·1015 = 0$

	CSA	ISA		CSA	ISA
O(1)*	−0·0056	0·0065	O(2)	−0·0061	−0·0049
N*	0·0069	0·0034	O(3)	0·0112	0·0029
C(1)*	−0·0023	−0·0070	C(3)	−0·0049	0·0130
C(2)*	−0·0035	−0·0024	C(6)	0·0320	0·0117
C(7)*	0·0087	0·0006	H(1)	0·044	−0·079
C(8)*	−0·0042	−0·0010			

The dihedral angles between the planes I and II are 0·95° for CSA and 0·64° for ISA.
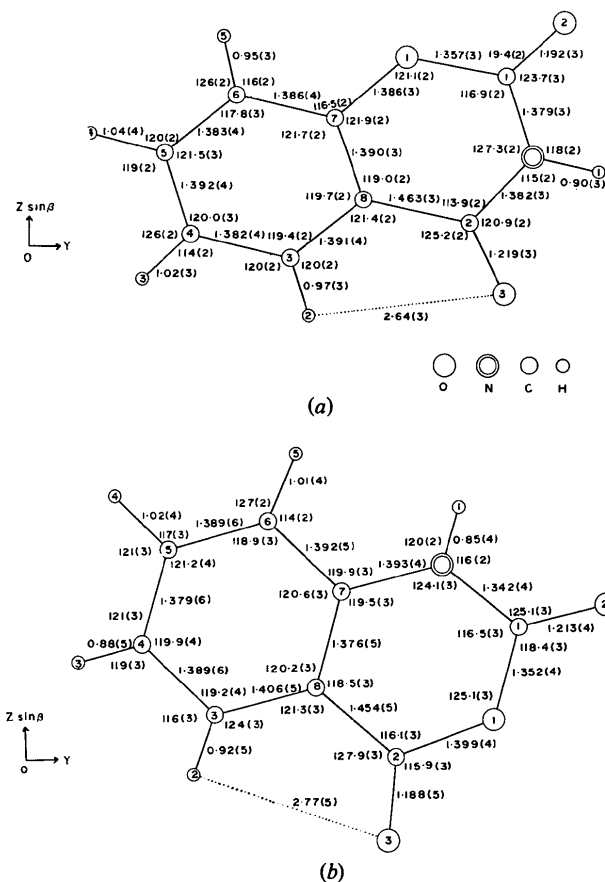
* Atoms used for calculation of the planes.

Fig. 1. Bond lengths (Å) and bond angles (°) for (a) CSA and (b) ISA, with e.s.d.'s in parentheses.

Table 5. Comparison of bond lengths (Å) in the hetero-rings of CSA and ISA with theoretical bond lengths derived from the simple HMO method

The π-bond order (p) and the bond length (r) are related by

$r(C-C) = 1\cdot517-0\cdot18p$ (Coulson & Golebiewski, 1961)
$r(C-O) = 1\cdot431-0\cdot257p$ (Häfelinger, 1970a)
$r(C-N) = 1\cdot460-0\cdot209p$ (Häfelinger, 1970b).

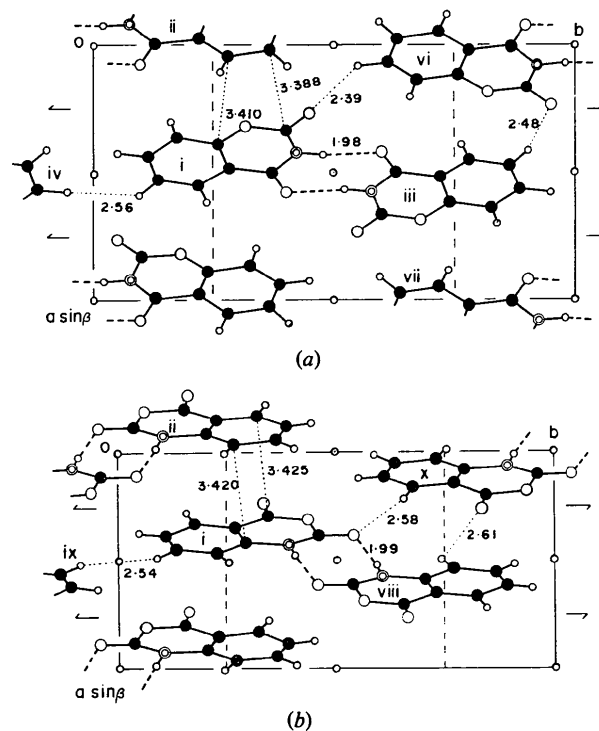| | CSA [X=C(7), Y=C(2)] | | ISA [X=C(2), Y=C(7)] | |
	Observed	Theoretical	Observed	Theoretical
O(1)—X	1·386 (3)	1·36	1·399 (4)	1·35
O(1)—C(1)	1·357 (3)	1·35	1·352 (4)	1·35
C(1)—N	1·379 (3)	1·38	1·342 (4)	1·38
Y—N	1·382 (3)	1·39	1·393 (4)	1·40
C(2)—C(8)	1·463 (3)	1·45	1·454 (5)	1·45
C(8)—C(7)	1·390 (3)	1·41	1·376 (5)	1·41
C(1)—O(2)	1·192 (3)	1·22	1·213 (4)	1·22
C(2)—O(3)	1·219 (3)	1·23	1·188 (5)	1·22

Fig. 2. Projections of the crystal structures of (a) CSA and (b) ISA along c. Broken lines show hydrogen bonds, and dotted lines intermolecular contacts. Symmetry code: (i) x,y,z; (ii) $-\frac{1}{2} + x$, $\frac{1}{2} - y$, z; (iii) $1 - x$, $1 - y$, $-z$; (iv) $1 - x$, $-y$, $-z$; (v) $x, y, 1 + z$; (vi) $\frac{1}{2} - x$, $\frac{1}{2} + y$, $1 - z$; (vii) $\frac{3}{2} - x$, $\frac{1}{2} + y$, $-1 - z$; (viii) $1 - x$, $1 - y$, $1 - z$; (ix) $1 - x$, $-y$, $1 - z$; (x) $\frac{1}{2} - x$, $\frac{1}{2} + y$, $-z$.

*sp*² hybridization. The C—N—C angles in both CSA and ISA are significantly larger than the *sp*² angle, consistent with the proposition of Singh (1965). From this fact and the lengths of the exocyclic C—O bond, it can be concluded that the ketonic form is the preferred tautomer in the crystals, in accordance with the results of an IR study (O'Sullivan & Sadler, 1957). The inner angle at N in CSA is larger than that in ISA, this probably being due to the difference in the number of C=O groups attached to N. Such a difference in the angles has also been observed in some six-membered heterocycles [lumazine hydrate (Norrestam, Stensland & Söderberg, 1972), and uracil (Stewart & Jensen, 1967)]. This is also the case for the inner angles at O in CSA and ISA.

The geometry of the C(ar)—O—CO system in CSA is similar to that found in coumarin derivatives (Shimizu, Kashino & Haisa, 1975). In this series of compounds the larger C(7)—O(1)—C(1) angles are associated with the longer O(1)—C(1) bonds. The geometry of the C(ar)—CO—NH—CO system is close to that found in lumazine hydrate.

Crystal structures

The crystal structures of CSA and ISA show an apparent resemblance in their molecular arrangement, as illustrated by the projections along c in Fig. 2. The molecules related by a centre of symmetry are linked

together by C=O···H—N hydrogen bonds [O···N 2·875 (3), O···H 1·98 (3) Å, $\angle$O···H—N 175 (3)° in CSA; O···N 2·830 (4), O···H 1·99 (4) Å, $\angle$O···H—N 172 (3)° in ISA] to form a dimer, in which the molecular planes are separated by 0·31 Å in CSA and 0·45 Å in ISA. The lengths of the C=O involved in the hydrogen bond are greater than the lengths of those
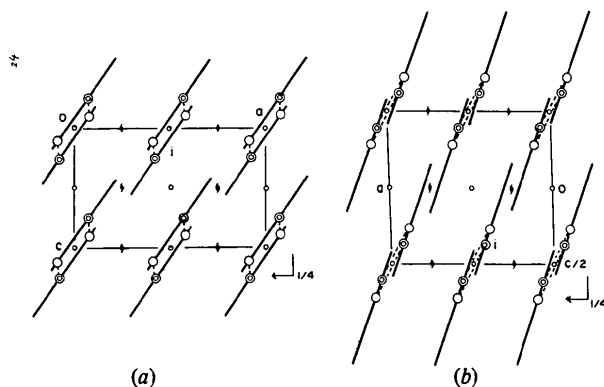

(a)   (b)

Fig. 3. Schematic view along b of the molecular arrangement in the crystals of (a) CSA and (b) ISA.
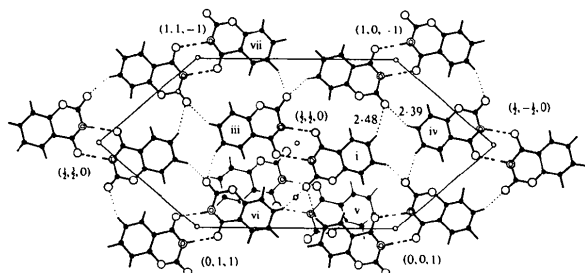

Fig. 4. Hexagonal arrangement of the centres of CSA dimers in the sheet, and overlapping of the molecules. The C—H···O interactions in the sheet are shown by dotted lines. The coordinates of the centres are shown in parentheses. See Fig. 2 for the symmetry code.

not involved, as pointed out for deoxyuridine and its related compounds (Rahman & Wilson, 1972).

The dimers related by twofold screw axes are held together by the C—H···O interactions to form a sheet parallel to planes (201) and ($\bar{2}$01) in CSA and ISA, respectively (shown schematically in Fig. 3). In CSA the molecules are arranged below and above the sheet alternately, while in ISA the molecules form stair-like steps in the sheet. In spite of minor differences, in the sheet each dimer is surrounded by six neighbours, whose centres form a hexagon elongated along b (as illustrated for CSA in Fig. 4). The coordinates of the centres for ISA are obtained simply by replacing $\frac{1}{2} - z$ for z in CSA.

The sheets are packed along c by van der Waals interactions: C(1)···O(3^v) 3·107 Å in CSA, H(5)···O(3^v) 2·75 Å in ISA. The molecules related by an a glide plane overlap nearly parallel. It should be noted that these compounds have rather high densities and melting points.

Morphotropism

Some characteristic features of the crystal and molecular structures of CSA and ISA are compared with those of isatin (IST) (Goldschmidt & Llewellyn, 1950) in Table 6. The degree of similarity ε_1 (Kitaigorodsky, 1961) between the monomeric units CSA, ISA and IST indicates that they are similar to one another and to phthalimide (PHI) (Matzat, 1972), an isomer of IST. Crystals of ISA are, in fact, isomorphous with those of IST, but are not strictly isomorphous with those of CSA. In PHI the sheet structure is not formed. The degree of similarity between the dimeric units of ISA and IST [ε_2(ISA/IST)] is remarkably high, in accordance with their isomorphism. ε_2(CSA/ISA) and ε_2(IST/PHI) are too low to allow discussion of the resemblance between the crystal structures of CSA/ISA and IST/PHI. The ratio of width to length of the rectangle (Arcos & Arcos, 1955) enclosing the dimeric unit serves as a

Table 6. *Comparison of characteristic features of the crystal and molecular structures*

	CSA	ISA	IST
Angle (°) between the molecular plane and the sheet plane	4	9	9
Angle (°) between the molecular plane and [010]	1·3	0·6	1
Dihedral angle (°) between the molecular planes related by a glide plane	2·5	1·4	1·5
Shortest C···C contact (Å) between the overlapping molecules	3·388	3·420	3·44
Degree of similarity of the monomeric units (ε_1)	0·95	0·85	0·88
	(to ISA)	(to IST)	(to PHI)
Degree of similarity of the dimeric units (ε_2)	0·60	0·81	0·64
	(to ISA)	(to IST)	(to PHI)
Ratio of width to length of the rectangle enclosing the dimeric unit	0·539	0·544	0·539
Circularity of the hexagon formed by the nearest neighbours	0·31	0·45	0·38
Angle (°) between b and the long axis of the dimeric unit	24	32	29

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

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

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 [01̄1] direction because of the geometric restriction of the dimeric unit, thus resulting in a ribbon instead of a sheet.

References

ARCOS, J. C. & ARCOS, M. (1955). Naturwissenschaften, 42, 608.

ASHIDA, T. (1973). The Universal Crystallographic Computing System - Osaka, The Computation Center, Osaka Univ.

COULSON, C. A. & GOLEBIEWSKI, A. (1961). Proc. Phys. Soc. 78, 1310–1320.

GOLDSCHMIDT, G. H. & LLEWELLYN, F. J. (1950). Acta Cryst. 3, 294–299.

HÄFELINGER, G. (1970a). Chem. Ber. 103, 2922–2940.

HÄFELINGER, G. (1970b). Chem. Ber. 103, 2941–2960.

International Tables for X-ray Crystallography (1962). Vol. III, pp. 202–203. Birmingham: Kynoch Press.

KASHINO, S. & HAISA, M. (1973). Bull. Chem. Soc. Jpn, 46, 1094–1098.

KITAIGORODSKY, A. I. (1961). Organic Chemical Crystallography, pp. 230–231. New York: Consultants Bureau.

MATZAT, E. (1972). Acta Cryst. B28, 415–418.

NORRESTAM, R., STENSLAND, B. & SÖDERBERG, E. (1972). Acta Cryst. B28, 659–666.

O'SULLIVAN, D. G. & SADLER, P. W. (1957). J. Chem. Soc. pp. 2916–2920.

RAHMAN, A. & WILSON, H. R. (1972). Acta Cryst. B28, 2260–2270.

SCHOLL, W. & CARSON, J. R. (1963). W. Va Acad. Sci. pp. 88–91.

SHIMIZU, S., KASHINO, S. & HAISA, M. (1975). Acta Cryst. B31, 1287–1292.

SINGH, C. (1965). Acta Cryst. 19, 861–864.

STEWART, R. F. & JENSEN, L. H. (1967). Acta Cryst. 23, 1102–1105.

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 ($C_{10}H_7N.C_6H_3N_3O_6$; FW 354·3) are monoclinic, $P2_1/n$, $a = 14\cdot37$ (1), $b = 15\cdot99$ (1), $c = 6\cdot682$ (4) Å, $\beta = 92\cdot17$ (5)°, $D_m = 1\cdot532$, $D_x = 1\cdot533$ 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, $a = 15\cdot528$ (8), $b = 15\cdot636$ (8), $c = 13\cdot102$ (6) Å, $\beta = 113\cdot56$ (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.

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