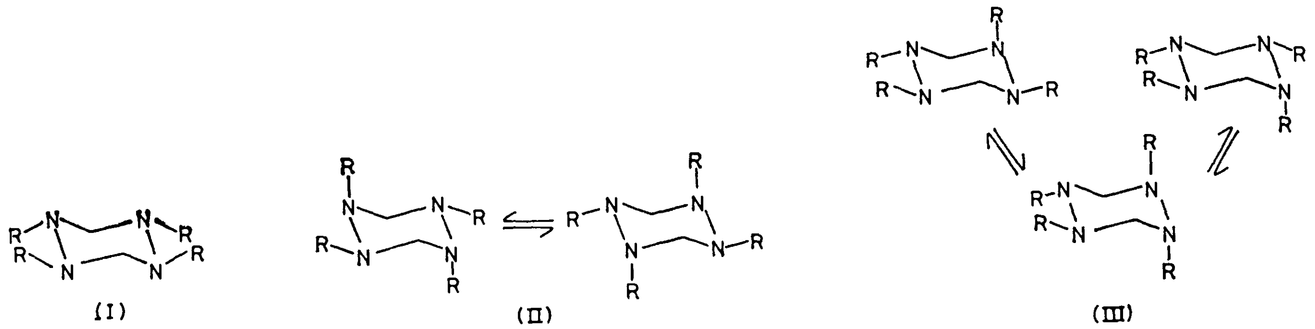
X-Ray Crystal Structures of 1,2,4,5-Tetra-azacyclohexanes: Molecular Dimensions for Examples of Three out of the Four Conformations existing in Solution[1]

By **Alan R. Katritzky** *,† and **Victor J. Baker**, School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ
Mercedes Camalli, Riccardo Spagna, and **Alessandro Vaciago**,* Laboratorio di Strutturistica Chimica ' G. Giacomello ' C.N.R., Casella Postale N.10, 00016 Monterotondo Stazione, Roma, Italy

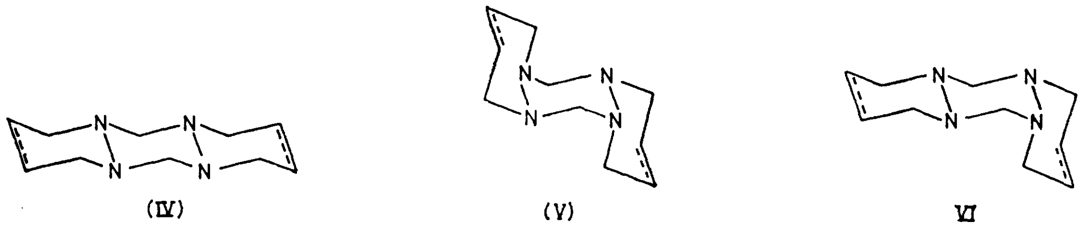
The 1,4-dimethyl-2,5-dibenzyl monocycle (2), the unsaturated tricycle (3), and the saturated tricycle (4) exist in the crystal in the *aeae*, ae_3, and e_4 conformations, respectively. The conformation behaviour is compared with that in solution and the molecular dimensions with those of similar compounds. The conformations deduced by n.m.r. spectroscopy for solutions are generally those found for the crystals.

THE conformational behaviour of several tetra-azacyclohexane systems, mono-, bi-, and tri-cyclic, has been extensively investigated, chiefly by means of ^{1}H and ^{13}C n.m.r. analysis, with supporting evidence from dipole moment and vibrational spectroscopy techniques.[2] The molecules were shown to exist in sets within which there is rapid interconversion, defined by higher energy barriers, and the results were rationalised in terms of steric, electronic, and entropy effects.[2]

Monocyclic



Tricyclic



SCHEME Conformational sets for tetra-azacyclohexanes (see ref. 1)

For most of the compounds the conclusions were unambiguous, but in the case of 1,2,4,5-tetrabenzyl-1,2,4,5-tetra-azacyclohexane (1) there was conflict between the n.m.r. evidence on one hand and dipole moment and vibrational spectroscopy on the other. The observed dipole moment (1.74 D) and high level of coincidences between the i.r. and Raman spectra (34 out of 40) suggested a non-centrosymmetric molecule, while the n.m.r. evidence pointed to the presence of the centrosymmetric sets (I) or (II) [probably (II)] (see Scheme). *X*-Ray analysis should help clarify the position, and such a study was therefore undertaken, of this tetrabenzyl compound, the dimethyl-dibenzyl compound (2), and the unsaturated and saturated tricyclic compounds (3) and (4). Together these were expected to show several different conformers of the tetra-azacyclohexane ring.

EXPERIMENTAL

The preparation of the compounds is described in refs. 2 and 3. Crystals of 2,5-dibenzyl-1,4-dimethyl-1,2,4,5-tetra-azacyclohexane (2) were grown from light petroleum (b.p. 40—60 °C) solution. 6*H*,13*H*-1,4,8,11-Tetrahydrobis-(pyridazino[1.2-α:1′,2′-*d*]-*s*-tetrazine) (3) was crystallised from water. The *X*-ray analysis showed that (3) contains one molecule of water per molecule of tetrazine compound. 6*H*,13*H*-Octahydrobis(pyridazino[1,2-*a*:1′,2′-*d*]-*s*-tetrazine) was obtained pure in form (4a) from ethyl acetate; crystal-

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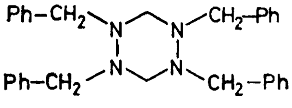
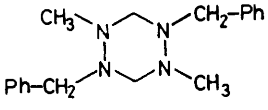
† *New permanent address:* Department of Chemistry, University of Florida, Gainesville, Florida, U.S.A.

lisation from tetrahydrofuran gave (4b) shown by *X*-ray analysis to contain one molecule of water and half a molecule of hydroquinone (which presumably originated as a stabilizer in the solvent) per molecule of tetrazine compound.

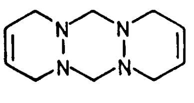
Preliminary Weissenberg photographs revealed that (2) is monoclinic (space group $P2_1/c$ from systematic absences), (3), (4a), and (4b) are triclinic (space group $P\bar{1}$ assumed on the basis of intensity statistics and later confirmed by the refinement).



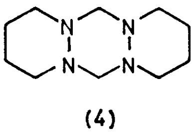
(1)



(2)



(3)



(4)

Lattice parameters and intensity measurements were performed on a Syntex $P2_1$ four-cycle computer-controlled diffractometer, using graphite monochromatised Mo-K_α radiation (λ 0.71069 Å), with crystals of dimension 0.4 × 0.35 × 0.2 mm, 0.5 × 0.4 × 0.1 mm, 0.3 × 0.3 × 0.1 mm, and 0.25 × 0.3 × 0.1 mm for (2), (3), (4a), and (4b), respectively. Crystal data are summarised in Table 1.

Intensity data were collected, for (2), (4a), and (4b) in the ω scan mode and for (3) in the θ–2θ scan mode, in the range 3° ⩽ 2θ ⩽ 56°, with a scan speed automatically chosen in the range 2—29.3° min^{-1} according to the peak intensity. The intensities of three standard reflections, monitored every 100 reflections, remained constant throughout the runs, showing no significant decay.

Of 3 365, 2 657, 1 733, and 3 581 independent reflections for (2), (3), (4a), and (4b), respectively, 1 394 [$F_o > 3\sigma(F_o)$] for (2), 1 631 [$F_o > 3\sigma(F_o)$] for (3), 899 [$I > 3\sigma(I)$] for (4a)], 1 610 [$F_o > 3\sigma(F_o)$] for (4b), were regarded as observed and used in the solution and refinement of the structure.

TABLE 1

Summary of crystal data of (2)—(4)

Formula	$N_4C_{18}H_{24}$	$N_4C_{10}H_{16},H_2O$	$N_4C_{10}H_{20}$	$N_4C_{10}H_{20}$, $\frac{1}{2}(C_6H_4(OH)_2)$,-$H_2O$
Molecular weight	296.4	210.3	196.3	269.4
a/Å	8.042(4)	6.482(2)	9.910(3)	11.040(6)
b/Å	12.693(6)	9.272(3)	5.287(1)	10.793(4)
c/Å	8.104(5)	10.403(3)	5.256(2)	6.973(2)
α (°)		106.24(2)	102.36(3)	101.73(3)
β (°)	99.33(5)	98.38(2)	92.89(3)	105.39(3)
γ (°)		109.60(2)	95.25(2)	104.70(3)
U/Å^3	816.3	545.3	267.2	741.5
D_m [a]/g cm^{-3}	1.19(1)	[b]	1.19(1)	[b]
Z	2	2	1	2
D_c/g cm^{-3}	1.206	1.281	1.220	1.206
Space group	C^5_{2h}–$P2_1/c$	C^1_i–$P\bar{1}$	C^1_i–$P\bar{1}$	C^1_i–$P\bar{1}$
μ(Mo-K_α)/cm^{-1}	0.69	0.81	0.72	0.78

[a] Measured by flotation in aqueous solutions. [b] The density was not measured due to the unusual solubility of the compound in most aqueous and organic solvents.

Intensities were corrected for Lorentz and polarisation effects.

Solution of the Structures.—Compounds (2), (3), *and* (4b). The phase problem was solved by routine application of the multiple-solution phasing procedure MULTAN.[4] The *E* maps calculated with the set of highest combined figure of merit revealed the positions of all non-hydrogen atoms. The structure-factor calculations based on those positions gave *R* values of 27, 37, and 21%, for (2), (3), and (4b), respectively.

Compound (4a). The structure was determined from a sharpened Patterson synthesis. The distribution of vector peaks suggested that the substituents at the nitrogen atoms are equatorial. An analysis of the distances and angles between the peaks as well as of their relative weights made it possible to recognise all the intramolecular vectors. Accordingly, all the non-hydrogen atoms were located and a structure factor calculation based on those positions gave a *R* value of 31%.

Refinement of the Structures.—All the structures were refined by least-squares methods [full-matrix for (2) and (4a), matrix reduced to suitable blocks for (3) and (4b)]. The isotropic refinement converged at *R* 19, 13, 14, and 13% for (2), (3), (4a), and (4b), respectively. At this stage for the four compounds all the hydrogen atoms, except those linked to the oxygen atoms in (3) and (4a), were positioned geometrically. Refinement was continued allowing all the non-hydrogen atoms to vibrate anisotropically. At the end of the refinement difference-Fourier maps for (3) and (4a) revealed the positions of the missing hydrogen atoms, whose contribution was included in the subsequent cycles. Convergence was reached at *R* 4.4, 6.4, 4.7, and 5.4% (*R'* 4.8, 7.7, 5.0, and 5.5%) for (2), (3), (4a), and (4b), repsectively. The final difference-Fourier maps, with a root-mean-square deviation of electron density of 0.05, 0.12, 0.06, and 0.07 e Å^{-3} respectively, have no significant features. The function minimised during refinement was $\Sigma w(|F_o| - |F_c|)^2$ with $w = \sin\theta/\lambda$ for (2), (3), and (4a) and $w = 1/\sigma^2(F_o)$ for (4b). Atomic scattering factors for neutral atoms were taken from ref. 5. Calculations were performed with MULTAN[4] and local programs[6] on the UNIVAC 1100/20 computer of the University of Rome and on the HP 21MX minicomputer of the CNR Computing Centre at U.E.A.

TABLE 2

Fractional co-ordinates ($\times 10^4$) for the non-hydrogen atoms of (2)—(4), with estimated standard deviations in parentheses

	x	*y*	*z*
Compound (2)			
N(1)	9 192(2)	280(1)	3 329(2)
N(2)	10 574(2)	−466(1)	3 685(2)
C(1)	9 414(2)	1 011(1)	4 727(2)
C(2)	7 487(2)	−201(1)	3 058(2)
C(3)	6 174(2)	578(1)	2 257(2)
C(4)	6 540(2)	1 348(2)	1 152(3)
C(5)	5 297(3)	2 031(2)	394(3)
C(6)	3 673(3)	1 947(2)	737(3)
C(7)	3 289(2)	1 187(2)	1 822(3)
C(8)	4 535(2)	503(2)	2 581(3)
C(9)	10 641(3)	−1 175(2)	2 284(3)
Compound (3)			
O(1)	1 690(6)	8 505(4)	1 976(3)
N(1)	−726(4)	3 985(3)	1 745(3)
N(2)	565(4)	3 174(3)	1 028(3)
N(3)	4 028(5)	5 469(3)	2 549(3)
N(4)	2 631(5)	6 246(3)	3 258(3)
C(1)	526(6)	4 922(4)	3 192(3)
C(2)	−2 982(6)	2 749(5)	1 559(4)
C(3)	−2 938(7)	1 229(5)	1 793(4)
C(4)	−1 122(7)	890(4)	1 811(4)
C(5)	1 007(6)	1 972(4)	1 591(4)
C(6)	2 649(6)	4 478(4)	1 105(3)
C(7)	6 013(6)	6 781(5)	2 480(4)
C(8)	7 254(8)	8 065(5)	3 879(4)
C(9)	6 278(8)	8 207(5)	4 903(4)
C(10)	3 899(8)	7 109(5)	4 732(4)
Compound (4a)			
N(1)	1 196(2)	671(3)	−1 151(3)
N(2)	1 138(2)	1 067(3)	1 722(3)
C(1)	254(2)	−1 598(4)	−2 265(4)
C(2)	2 570(2)	4(5)	−1 778(5)
C(3)	3 597(2)	2 291(5)	−598(5)
C(4)	3 481(3)	3 069(6)	2 334(5)
C(5)	2 013(2)	3 450(5)	2 911(4)
Compound (4b)			
C(1)	831(4)	140(3)	−1 106(5)
N(1)	1 118(3)	−422(2)	641(4)
N(2)	−196(3)	−1 147(2)	698(4)
C(2)	1 761(4)	−1 438(3)	109(6)
C(3)	2 031(4)	−2 091(4)	1 823(6)
C(4)	753(4)	−2 707(4)	2 204(7)
C(5)	34(5)	−1 691(4)	2 504(6)
C(6)	4 414(3)	4 620(3)	2 910(4)
N(3)	3 610(2)	4 336(2)	4 230(3)
N(4)	4 267(2)	5 452(2)	6 191(3)
C(7)	2 286(3)	4 423(3)	3 226(5)
C(8)	1 433(4)	4 239(4)	4 588(6)
C(9)	2 121(4)	5 254(4)	6 719(6)
C(10)	3 513(3)	5 198(3)	7 607(5)
C(11)	4 531(3)	−155(3)	7 896(5)
C(12)	4 545(3)	966(3)	9 289(5)
C(13)	5 025(3)	1 119(3)	11 395(5)
O(1)	4 089(3)	1 946(2)	8 666(4)
O(2)	2 986(3)	1 615(3)	4 607(4)

Table 2 lists the final co-ordinates of the non-hydrogen atoms for the four compounds.*

RESULTS AND DISCUSSION

The structures of the compounds are shown in Figures 1—4 together with the numbering scheme adopted. Bond lengths, valence angles, and a selection of torsion angles [7] are given in Tables 3—6. In all the compounds, the tetrazine ring has a chair conformation.

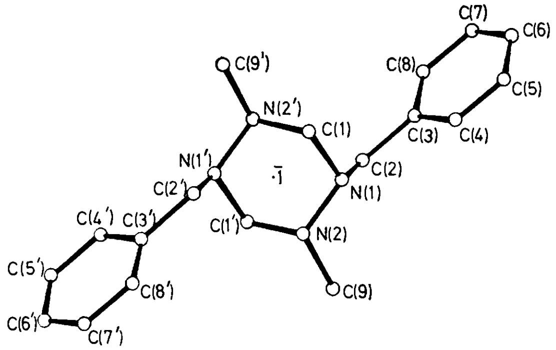


FIGURE 1 Perspective view of compound (2). Atom numbering scheme and the centre of symmetry are indicated

Conformations in the crystal can differ from those in solution.

TABLE 3

Intramolecular bond lengths (Å), valence angles (°), and a selection of torsion angles (°), with estimated standard deviations in parentheses, for compound (2)

(*a*) Bond distances

N(1)–N(2)	1.453(2)	C(3)–C(4)	1.389(3)
N(1)–C(1)	1.453(2)	C(3)–C(8)	1.389(2)
N(1)–C(2)	1.484(2)	C(4)–C(5)	1.389(3)
N(2)–C(1′)	1.459(2)	C(5)–C(6)	1.383(3)
N(2)–C(9)	1.457(3)	C(6)–C(7)	1.373(3)
C(2)–C(3)	1.514(3)	C(7)–C(8)	1.391(3)

(*b*) Valence angles

N(1)–C(1)–N(2′)	111.5(1)	C(2)–C(3)–C(4)	122.0(2)
C(1)–N(1)–N(2)	105.6(1)	C(2)–C(3)–C(8)	119.4(2)
N(1)–N(2)–C(1′)	112.3(1)	C(4)–C(3)–C(8)	118.5(2)
C(1)–N(1)–C(2)	111.8(1)	C(3)–C(4)–C(5)	120.8(2)
N(2)–N(1)–C(2)	114.9(1)	C(4)–C(5)–C(6)	119.9(2)
N(1)–N(2)–C(9)	111.8(2)	C(5)–C(6)–C(7)	120.1(2)
C(1′)–N(2)–C(9)	113.5(2)	C(6)–C(7)–C(8)	120.1(2)
N(1)–C(2)–C(3)	111.0(2)	C(7)–C(8)–C(3)	120.7(2)

(*c*) Torsion angles

C(1)–N(1)–N(2)–C(1′)	58.3(2)
N(1)–N(2)–C(1′)–N(1′)	−61.8(2)
N(2)–C(1′)–N(1′)–N(2′)	57.8(2)
C(2)–N(1)–N(2)–C(1′)	−65.4(2)
C(2)–N(1)–N(2)–C(9)	63.5(2)
C(2)–N(1)–C(1)–N(2′)	67.8(2)
C(1)–N(1)–N(2)–C(9)	−172.8(2)
N(1′)–C(1′)–N(2)–C(9)	170.2(2)

1,2,4,5-*Tetrabenzyl*-1,2,4,5-*tetra-azacyclohexane* (1).—The n.m.r. work suggested that this compound exists in the centrosymmetric diaxial diequatorial form [set (II)].

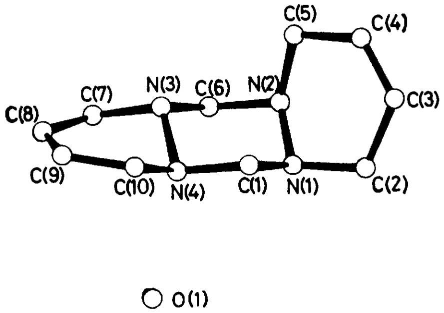


FIGURE 2 Perspective view of compound (3). Atom numbering scheme is indicated

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* Tables of anisotropic thermal parameters for non-hydrogen atoms, positional and thermal parameters for hydrogen atoms, and lists of structure factors for the four compounds are given in Supplementary Publication No. SUP 22830 (43 pp.). For details see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1979, Index Issue.

A previously published [8] *X*-ray study fully confirms this for the solid state.

1,4-*Dimethyl*-2,5-*dibenzyl*-1,2,4,5-*tetra-azacyclohexane* (2).—The *X*-ray work shows that in the crystal set (II) alone is adopted: the tetrazine ring shows the *aeac* conformation with the benzyl and methyl groups in axial and equatorial positions respectively. The previous work had disclosed a more complex situation for solutions, a mixture in which the non-centrosymmetric set (III) predominated (67%) together with 33% of a centrosymmetric set, which was thought to be (II) [but could have been (I)]. Interestingly, the benzyl groups are axial while the methyl groups are equatorial, an

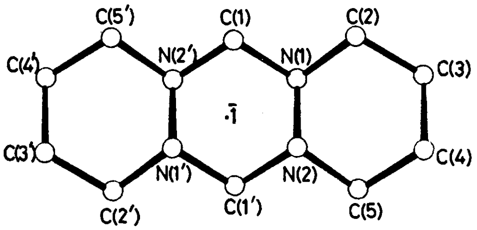


FIGURE 3 Perspective view of the compound (4a). Atom numbering scheme and the centre of symmetry are indicated

TABLE 4

Intramolecular bond lengths (Å), valence angles (°), and a selection of torsion angles (°), with estimated standard deviations in parentheses, for compound (3)

(*a*) Bond distances

N(1)–N(2)	1.453(4)	N(3)–N(4)	1.489(4)
N(1)–C(1)	1.456(6)	N(3)–C(6)	1.478(6)
N(1)–C(2)	1.469(6)	N(3)–C(7)	1.472(6)
N(2)–C(5)	1.483(4)	N(4)–C(1)	1.475(6)
N(2)–C(6)	1.453(6)	N(4)–C(10)	1.474(7)
C(2)–C(3)	1.504(6)	C(7)–C(8)	1.494(8)
C(3)–C(4)	1.315(6)	C(8)–C(9)	1.314(6)
C(4)–C(5)	1.501(7)	C(9)–C(10)	1.487(9)

(*b*) Valence angles

N(1)–C(1)–N(4)	109.2(3)	C(2)–C(3)–C(4)	121.3(4)
C(1)–N(1)–N(2)	110.3(3)	C(3)–C(4)–C(5)	122.6(4)
N(1)–N(2)–C(6)	105.6(3)	C(4)–C(5)–N(2)	110.5(3)
N(2)–C(6)–N(3)	112.6(3)	C(6)–N(3)–C(7)	107.0(3)
C(6)–N(3)–N(4)	106.7(3)	N(4)–N(3)–C(7)	107.7(3)
N(3)–N(4)–C(1)	107.5(3)	C(1)–N(4)–C(10)	107.4(3)
C(1)–N(1)–C(2)	113.8(3)	N(3)–N(4)–C(10)	107.2(3)
N(2)–N(1)–C(2)	108.6(3)	N(3)–C(7)–C(8)	111.4(3)
N(1)–N(2)–C(5)	114.0(3)	C(7)–C(8)–C(9)	121.2(6)
C(6)–N(2)–C(5)	112.3(3)	C(8)–C(9)–C(10)	122.0(6)
N(1)–C(2)–C(3)	114.1(3)	C(9)–C(10)–N(4)	111.9(3)

(*c*) Torsion angles

C(1)–N(1)–N(2)–C(6)	−61.6(4)
N(1)–N(2)–C(6)–N(3)	62.0(4)
N(2)–C(6)–N(3)–N(4)	−62.2(4)
C(6)–N(3)–N(4)–C(1)	59.5(4)
N(3)–N(4)–C(1)–N(1)	−62.1(4)
N(4)–C(1)–N(1)–N(2)	64.4(4)
C(2)–N(1)–N(2)–C(6)	173.1(3)
C(2)–N(1)–N(2)–C(5)	−63.2(3)
C(2)–N(1)–C(1)–N(4)	−173.4(4)
C(5)–N(2)–N(1)–C(1)	62.1(3)
C(5)–N(2)–C(6)–N(3)	−62.8(4)
C(7)–N(3)–N(4)–C(1)	174.0(3)
C(7)–N(3)–N(4)–C(10)	−70.8(4)
C(7)–N(3)–C(6)–N(2)	−177.3(3)
C(10)–N(4)–N(3)–C(6)	174.7(3)
C(10)–N(4)–C(1)–N(1)	−177.2(4)

TABLE 5

Intramolecular bond lengths (Å), valence angles (°), and a selection of torsion angles (°), with estimated standard deviations in parentheses, for compound (4a)

(*a*) Bond distances

N(1)–N(2)	1.484(2)	N(2)–C(5)	1.462(3)
N(1)–C(1)	1.446(3)	C(2)–C(3)	1.507(4)
N(1)–C(2)	1.473(3)	C(3)–C(4)	1.520(4)
N(2)–C(1′)	1.463(3)	C(4)–C(5)	1.523(3)

(*b*) Valence angles

N(1)–C(1)–N(2′)	110.4(2)	C(1′)–N(2)–C(5)	106.6(2)
C(1)–N(1)–N(2)	105.9(2)	N(1)–C(2)–C(3)	109.6(2)
N(1)–N(2)–C(1′)	106.0(2)	C(2)–C(3)–C(4)	110.0(2)
C(1)–N(1)–C(2)	107.5(2)	C(3)–C(4)–C(5)	110.1(2)
N(2)–N(1)–C(2)	107.4(2)	C(4)–C(5)–N(2)	109.5(2)
N(1)–N(2)–C(5)	107.4(2)		

(*c*) Torsion angles

C(1)–N(1)–N(2)–C(1′)	−62.7(2)
N(1)–N(2)–C(1′)–N(1′)	65.8(4)
N(2)–C(1′)–N(1′)–N(2′)	−65.7(4)
C(2)–N(1)–N(2)–C(1′)	−177.3(2)
C(2)–N(1)–N(2)–C(5)	69.1(2)
C(2)–N(1)–C(1)–N(2′)	−179.8(4)
C(1)–N(1)–N(2)–C(5)	−176.4(2)
N(1′)–C(1′)–N(2)–C(5)	180.0(4)

TABLE 6

Intramolecular bond lengths (Å), valence angles (°), and a selection of torsion angles (°), with estimated standard deviations in parentheses, for compound (4b)

(*a*) Bond distances

N(1)–N(2)	1.478(4)	N(3)–C(7)	1.479(5)
N(1)–C(1)	1.464(4)	N(4)–C(6′)	1.453(5)
N(1)–C(2)	1.488(4)	N(4)–C(10)	1.474(4)
N(2)–C(1′)	1.457(4)	C(7)–C(8)	1.512(5)
N(2)–C(5)	1.484(5)	C(8)–C(9)	1.517(8)
C(2)–C(3)	1.509(5)	C(9)–C(10)	1.519(6)
C(3)–C(4)	1.516(7)	O(1)–C(12)	1.378(4)
C(4)–C(5)	1.521(6)	C(11)–C(12)	1.383(5)
N(3)–N(4)	1.486(4)	C(11)–C(13′)	1.381(4)
N(3)–C(6)	1.463(4)	C(12)–C(13)	1.382(5)

(*b*) Valence angles

N(1)–C(1)–N(2′)	110.9(3)	C(6)–N(3)–C(7)	107.8(2)
C(1)–N(1)–N(2)	105.2(3)	N(4)–N(3)–C(7)	107.6(2)
N(1)–N(2)–C(1′)	106.0(3)	N(3)–N(4)–C(10)	107.7(3)
C(1)–N(1)–C(2)	107.7(3)	C(6′)–N(4)–C(10)	108.5(3)
N(2)–N(1)–C(2)	107.2(3)	N(3)–C(7)–C(8)	110.7(3)
N(1)–N(2)–C(5)	107.6(3)	C(7)–C(8)–C(9)	110.6(4)
C(1′)–N(2)–C(5)	107.8(3)	C(8)–C(9)–C(10)	109.1(3)
N(1)–C(2)–C(3)	110.0(3)	C(9)–C(10)–N(4)	110.3(3)
C(2)–C(3)–C(4)	110.2(4)	O(1)–C(12)–C(11)	122.7(3)
C(3)–C(4)–C(5)	110.5(4)	O(1)–C(12)–C(13)	118.0(3)
C(4)–C(5)–N(2)	110.1(3)	C(11)–C(12)–C(13)	119.3(3)
N(3)–C(6)–N(4′)	110.7(3)	C(12)–C(13)–C(11′)	120.4(4)
C(6)–N(3)–N(4)	105.4(3)	C(12)–C(11)–C(13′)	120.3(4)
N(3)–N(4)–C(6′)	106.4(2)		

(*c*) Torsion angles

C(1)–N(1)–N(2)–C(1′)	−62.5(3)
N(1)–N(2)–C(1′)–N(1′)	66.3(3)
N(2)–C(1′)–N(1′)–N(2′)	−65.9(3)
C(2)–N(1)–N(2)–C(1′)	−176.9(3)
C(2)–N(1)–N(2)–C(5)	68.0(3)
C(2)–N(1)–C(1)–N(2′)	179.9(2)
C(1)–N(1)–N(2)–C(5)	−177.6(3)
N(1′)–C(1′)–N(2)–C(5)	−178.7(2)
C(6)–N(3)–N(4)–C(6′)	−62.5(3)
N(3)–N(4)–C(6′)–N(3′)	66.0(3)
N(4)–C(6′)–N(3′)–N(4′)	−65.4(3)
C(7)–N(3)–N(4)–C(6′)	−177.3(3)
C(7)–N(3)–N(4)–C(10)	66.5(3)
C(7)–N(3)–C(6)–N(4′)	−179.9(2)
C(6)–N(3)–N(4)–C(10)	−178.6(3)
N(3′)–C(6′)–N(4)–C(10)	−178.4(2)

inversion of the steric preference usually considered to apply.

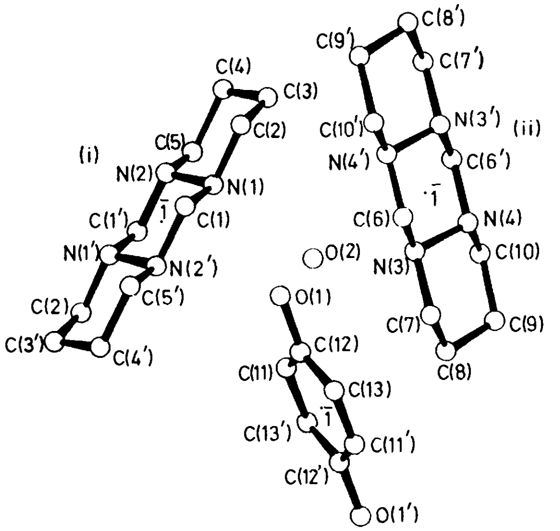
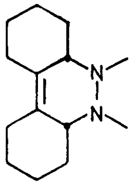


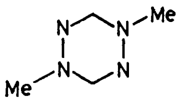
FIGURE 4 Perspective view of compound (4b). Atom numbering scheme and the centres of symmetry are indicated

6H,13H-1,4,8,11-*Tetrahydrobis(pyridazino*[1,2-a:1',2'-d]-s-*tetrazine*) (3).—In solution the conformational picture is complex: all the possible sets (IV)—(VI) [in the tricycle analogous to sets (I)—(III) of the monocycles, see Scheme] are populated, respectively in the proportions 13, 20, and 67%. The X-ray analysis shows the exclusive presence of set (VI) (*acee*) in the crystal, *i.e.* the set which also dominates the equilibrium in solution.

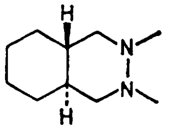
6H,13H-*Octahydrobis(pyridazino*[1,2-a:1',2'-d]-s-*tetrazine*) (4).—Here the n.m.r. work had demonstrated



(5)



(6)



(7)

the all-equatorial form (IV) to be present exclusively, and unsurprisingly this is found also to be the case in the crystalline state from the X-ray work.

Bond Lengths and Angles.—In Table 7 the relevant geometrical features observed in the tetrazine ring of these compounds are compared with those observed in other similar compounds.

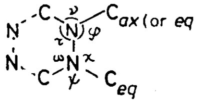
The N–N bond length seems to depend on the conformation of the hydrazine unit. The mean values are 1.484 and 1.451 Å for the *ee* and *ae* conformations respectively and the two values differ significantly. The shorter one is in good agreement with the value observed in hydrazine [1.453(5) Å by i.r. technique,[9] 1.449(4) Å by electron diffraction analysis [10]]. The longer value is observed in the *ee* conformation for which the lone pair–lone pair energy separation is higher than in the *ae* conformation.[11]

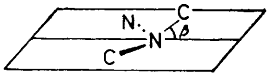
TABLE 7

A comparison of the relevant geometrical features observed in the tetrazine ring in similar compounds

	N–N (Å)	N–C_{ax} [a] (Å)	N–C_{eq} [a] (Å)	τ (°)	ν (°)	ϕ (°)	χ (°)	ψ (°)	ω (°)	β_{ax} (°)	β_{eq} (°)
aeae											
(1) [b]	1.452(5)	$1.494(5)^{ii}$	$1.472(5)^{ii}$	105.7(3)	111.6(3)	114.4(3)	111.6(4)	114.3(3)	112.3(3)	49.6	45.6
(2)	1.453(2)	$1.484(2)^{ii}$	$1.457(3)^{i}$	105.6(1)	111.8(1)	114.9(1)	111.8(2)	113.5(2)	112.3(1)	49.1	46.3
(5) [c,d]	1.450(3)	$1.466(4)^{i}$	$1.463(4)^{i}$	107.3(2)	111.5(2)	113.9(2)	109.3(2)	114.0(2)	113.3(2)	49.4	47.8
(6) [e]	1.447(3)		$1.460(4)^{i}$								
aeee											
(3)	1.453(4)	$1.483(4)^{iii}$	$1.469(6)^{iii}$	105.6(3)	112.3(3)	114.0(3)	108.6(3)	113.8(3)	110.3(3)	49.4	50.7
	1.489(4)		$1.472(6)^{iii}$	106.7(3)	107.0(3)	107.7(3)	107.2(3)	107.4(3)	107.5(3)		59.9
			$1.474(7)^{iii}$								60.0
eeee											
(4a)	1.484(2)		$1.462(3)^{iii}$	105.9(2)	107.5(2)	107.4(2)	107.4(2)	106.6(2)	106.0(2)		60.2
			$1.473(3)^{iii}$								60.9
(4b) (i)	1.478(4)		$1.488(4)^{iii}$	105.2(3)	107.7(3)	107.2(3)	107.6(3)	107.8(3)	106.0(3)		60.4
			$1.484(5)^{iii}$								59.6
(4b) (ii)	1.486(4)		$1.479(5)^{iii}$	105.4(3)	107.8(2)	107.6(2)	107.7(3)	108.5(3)	106.4(2)		59.9
			$1.474(4)^{iii}$								58.8
(7)	1.486(4)		$1.468(5)^{i}$	107.7(3)	107.2(4)	108.2(4)	108.1(4)	107.5(4)	106.5(3)		59.0
			$1.464(6)^{i}$								59.3

[a] Superscripts of the values of bond lengths denote that the C atom is referred to the methyl group, *i*; to the benzyl group, *ii*; and to the external ring, *iii*. τ—ω are the angles at the nitrogen atoms as shown:





β is the angle of bend of the N-substituent group out of the CNN' plane (54.7° for a tetrahedral atom). [b] Ref. 8. [c] S. F. Nelsen, W. C. Hollinsed, and J. C. Calabrese, *J. Amer. Chem. Soc.*, 1977, **99**, 4461. [d] However the comparison of (6) with the others is poor (a) because one of the hydrazine nitrogen atoms carries no substituents and (b) because of the strong intermolecular hydrogen bonding observed. [e] G. B. Ansell and J. L. Erickson, *J.C.S. Perkin II*, 1975, 270.

The values of the angles at the nitrogen atoms show a trend which is in accordance with the difference observed in the N–N bond lengths. For hydrazine units in the *ae* conformation, larger values for the angles are observed, denoting that the tetrahedrons around the nitrogen atoms are flattened. The opposite trend is shown by the values of the angles observed for hydrazine units with the *ee* conformations. The degree of flattening may be indicated by the values of β (the bending angle of the substituent), which in units with the *ae* conformation is five or more degrees lower than the theoretical value, while it is about five degrees higher in units with the *ee* conformation.

These differences show that the hybrid atomic orbitals with which the nitrogen atom forms bonds have more *s* character in the *ae* conformation than in the *ee* conformation. Consequently the lone pairs of the nitrogen atoms in *ee* conformation are in orbitals with higher *s* character.

For the N–C bond lengths the observed values range between 1.457(3) and 1.494(5) Å. The limiting values are significantly different and it seems that the *N*-benzyl bond lengths fall in the highest region of the range, while the *N*-methyl bond lengths fall in the lowest region.

Bond lengths and bond angles of the phenyl group in (2) and of the hydroquinone molecule in (4b) are in good agreement with the accepted values for C–C and C–O distances.

No short intermolecular contacts are observed in (2) and (4a). In crystals of (3) there exists an extended network of hydrogen bonds which involves the solvent molecules. In (4b) the molecules of the tetrazine derivative and those of the solvents are connected by hydrogen bonds. Table 8 reports the hydrogen-bond distances in (3) and (4b).

TABLE 8

Hydrogen bond distances (Å)

X–H · · · Y	X · · · Y	X–H · · · Y	X · · · Y
Compound (3)			
O(1)–H · · · N(2) [a]	2.958(6)	O(1)–H · · · N(4)	2.952(4)
Compound (4b)			
O(2)–H · · · N(1)	2.989(6)	O(1)–H · · · O(2)	2.676(5)
O(2)–H · · · N(3)	2.924(4)		

[a] $-x, 1 - y, -z$.

Conclusions.—Crystals will normally comprise isomorphic molecules and the exclusive existence of a single conformer for each compound shown by the above *X*-ray results is to be expected. Where a single set was found to exist in solution, this has been reflected in the crystal conformation [(1) and (4)].

The results in the case of the tetrabenzyl compound (1) confirm the earlier supposition [2] that the n.m.r. results were to be preferred to those of dipole moments and vibrational spectroscopy. Whether the discrepancy is really due to solvent differences or perhaps the excessive sensitivity of the latter techniques to experimental difficulty or impurity is still not completely clear. However, the experiments using different solvents suggested that this was unlikely to be the cause, whereas we have reason to believe that dipole moment results should be treated with care.*

For two of the compounds investigated the solution work had demonstrated a mixture of conformations: the tricycle (3) exists in the crystal in the conformation that dominates in solution. However the dimethyldibenzyl derivative crystallises in the conformation corresponding to a minor (33%) component of the solution equilibrium.

The present work makes available the molecular dimensions of examples of three of the four conformations open to tetra-azacyclohexanes: e_4, ae_3, and symmetrical a_2e_2: we have as yet no example for the remaining unsymmetrical a_2e_2 conformation.

[9/1891 *Received, 28th November*, 1979]

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* A critical analysis of the dipole moment work is currently in progress.

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