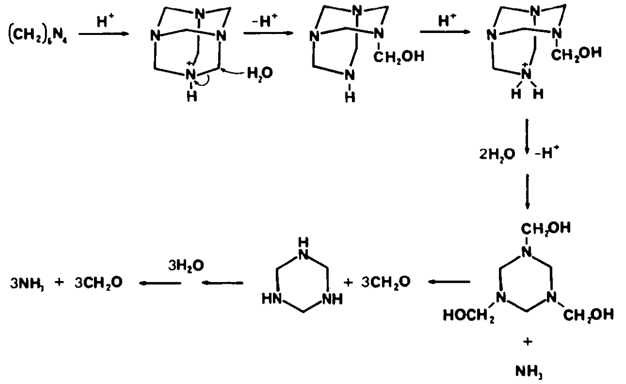
attack of a water molecule on the α-carbon atom, as illustrated in the scheme below.



The present crystal structure (Fig. 2), which is isostructural with those of $(CH_2)_6N_4.BH_3$ and $(CH_2)_6N_4O$, can be derived from a cubic unit cell of hexamethylenetetramine (space group $I\bar{4}3m$, $Z = 2$) by first removing the $(CH_2)_6N_4$ molecule at the body-center, then introducing the proton and $Br^-$ ion in the [111] direction to each remaining molecule, and finally extending the resulting primitive rhombohedral lattice along [111] until optimum packing is achieved. The observed N(1)···Br separation of 3·173 (5) Å is in good agreement with the mean value of 3·37 (15) Å for weak hydrogen bonds of the type $N—N^+\cdots Br^-$ (Joesten & Schaad, 1974). All van der Waals contacts of $Br^-$ with neighboring C and H atoms are longer than 3·80 and 3·02 Å, respectively.

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# Structure of 2,3-Diphenylpyrazine, $C_{16}H_{12}N_2$

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**Abstract.** $M_r = 232{\cdot}28$, monoclinic, $C2/c$, $a = 25{\cdot}849$ (4), $b = 10{\cdot}277$ (4), $c = 19{\cdot}011$ (3) Å, $\beta = 97{\cdot}51$ (1)°, $V = 5007{\cdot}0$ Å$^3$, $D_x = 1{\cdot}233$ Mg m$^{-3}$, $Z = 16$, $F(000) = 1952$, $\mu$ (Cu $K\alpha$) = 0·58 mm$^{-1}$. The final $R$ was 0·0605 for 4149 unique reflections. Each of the two independent molecules has approximate 2 ($C_2$) symmetry and the molecular geometries are nearly the same; the two pyrazine rings are essentially planar and the dihedral angles between the two phenyl substituents and the pyrazine rings are 51·4 and 40·2° for one molecule and 51·0 and 38·0° for the other.

**Introduction.** Since pyrazine derivatives are of interest due to their pharmacological activity and natural occurrence (Sammes, 1975; Cheeseman & Werstiuk, 1972), syntheses and reactivities of a series of pyrazines

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have been studied by the authors (Akita & Ohta, 1982). The peculiar reactivity of 2,3-diphenylpyrazine 1-oxide prompted us to investigate the molecular structure of the parent amine by $^{13}$C NMR and the charge density study by the CNDO/2 method (Ohta, Masano, Iwakura, Tamura, Watahiki, Tsutsui, Akita & Watanabe, 1982; Matsuo, Matsumoto, Kurihara, Akita, Watanabe & Ohta, 1980). The crystal structure determination of the compound was undertaken to provide necessary information to complement the above studies.

**Experimental.** The compound was synthesized by the method previously reported (Ohta *et al.*, 1982), and recrystallized by slow evaporation of a hexane solution to give colorless plates elongated along **b**. Preliminary Weissenberg photographs showed the crystal to be monoclinic, *Cc* or *C*2/*c*. Centrosymmetric *C*2/*c* was later selected as the correct space group on the basis of the distribution of normalized structure factors. Data collection: Rigaku four-circle diffractometer, graphite-monochromated Cu $K\alpha$ radiation; single crystal, 0·25 × 0·35 × 0·15 mm, mounted with **b** coincident with the goniostat axis; unit-cell dimensions determined by least-squares refinement of angular settings of 13 reflections; intensities measured at room temperature, $2\theta$–$\omega$ scan, scan rate $10°(\omega)\,\mathrm{min}^{-1}$ with $\Delta\omega = (0{\cdot}8 + 0{\cdot}142\tan\theta)°$; three standard reflections measured periodically, no significant change in intensities; 4149 (3896 non-zero) unique reflections collected up to $2\theta = 128°$; corrected for Lorentz–polarization, not for absorption; direct methods (*MULTAN*78; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), block-diagonal least-squares procedure (*HBLS* V; Ashida, 1973), anisotropic temperature factors for non-H atoms, isotropic for H. Since there are 16 molecules in the cell with space group *C*2/*c*, two independent molecules are in the asymmetric unit. The first *E* map calculated using 244 $|E| > 1{\cdot}9$ revealed all non-H atoms; H atoms found at or near calculated positions in a difference Fourier map after a few cycles of anisotropic refinement. Function minimized: $\sum w(|F_o| - |F_c|)^2$ with $w = [\sigma^2(F_o) + a|F_o| + b|F_o|^2]^{-1}$ for $F_o \neq 0$ and $w = c$ for $F_o = 0$, where $\sigma(F_o)$ is the standard deviation based on counting statistics. Final refinement ($a = -0{\cdot}0663$, $b = 0{\cdot}0032$, $c = 0{\cdot}2363$) gave $R$ 0·0605 for all reflections and $R = 0{\cdot}0554$ for non-zero reflections. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Final atomic parameters are in Table 1.*

**Discussion.** Molecular structures with the atom-numbering scheme, interatomic bond distances and

Table 1. *Fractional atomic coordinates* ($\times 10^4$; *for* H $\times 10^3$), $B_{eq}$ *values for non-*H *atoms* ($\times 10^2$) *and isotropic thermal parameters for* H *atoms* ($\times 10$) *with e.s.d.'s in parentheses*

Each H atom is numbered according to the C atom to which it is bonded. The $B_{eq}$ values are derived after Hamilton (1959).

| | $x$ | $y$ | $z$ | $B_{eq}$,$B$(Å$^2$) |
|---|---|---|---|---|
| Molecule *A* | | | | |
| N(1) | 1232 (1) | 577 (2) | 7481 (1) | 386 (6) |
| N(2) | 1417 (1) | −1965 (2) | 7930 (1) | 408 (6) |
| C(1) | 1489 (1) | −247 (2) | 7106 (1) | 312 (5) |
| C(2) | 1607 (1) | −1515 (2) | 7351 (1) | 321 (6) |
| C(3) | 1139 (1) | −1147 (2) | 8277 (1) | 440 (8) |
| C(4) | 1063 (1) | 126 (2) | 8067 (1) | 433 (7) |
| C(5) | 1612 (1) | 270 (2) | 6415 (1) | 328 (6) |
| C(6) | 1845 (1) | 1477 (2) | 6385 (1) | 466 (8) |
| C(7) | 1931 (1) | 2000 (2) | 5735 (1) | 548 (10) |
| C(8) | 1781 (1) | 1318 (2) | 5114 (1) | 506 (9) |
| C(9) | 1552 (1) | 117 (2) | 5146 (1) | 460 (8) |
| C(10) | 1468 (1) | −406 (2) | 5793 (1) | 378 (7) |
| C(11) | 1940 (1) | −2451 (2) | 7023 (1) | 332 (6) |
| C(12) | 2397 (1) | −2074 (2) | 6772 (1) | 380 (7) |
| C(13) | 2713 (1) | −2993 (2) | 6503 (1) | 473 (8) |
| C(14) | 2572 (1) | −4287 (2) | 6481 (1) | 507 (9) |
| C(15) | 2119 (1) | −4667 (2) | 6725 (1) | 524 (9) |
| C(16) | 1799 (1) | −3763 (2) | 7000 (1) | 438 (8) |
| H(3) | 99 (1) | −153 (2) | 871 (1) | 30 (5) |
| H(4) | 87 (1) | 73 (2) | 835 (1) | 35 (5) |
| H(6) | 197 (1) | 193 (3) | 681 (1) | 41 (6) |
| H(7) | 214 (1) | 282 (3) | 572 (1) | 48 (7) |
| H(8) | 186 (1) | 173 (3) | 465 (1) | 45 (6) |
| H(9) | 143 (1) | −28 (3) | 472 (1) | 52 (7) |
| H(10) | 128 (1) | −122 (2) | 583 (1) | 22 (4) |
| H(12) | 251 (1) | −116 (2) | 682 (1) | 25 (5) |
| H(13) | 304 (1) | −275 (2) | 639 (1) | 33 (5) |
| H(14) | 281 (1) | −494 (2) | 630 (1) | 36 (5) |
| H(15) | 202 (1) | −550 (2) | 671 (1) | 41 (6) |
| H(16) | 145 (1) | −396 (2) | 715 (1) | 30 (5) |
| Molecule *B* | | | | |
| N(1) | 188 (1) | 7323 (2) | 3635 (1) | 474 (7) |
| N(2) | −536 (1) | 5379 (2) | 3241 (1) | 542 (8) |
| C(1) | 307 (1) | 6071 (2) | 3768 (1) | 356 (6) |
| C(2) | −69 (1) | 5097 (2) | 3606 (1) | 389 (7) |
| C(3) | −636 (1) | 6625 (2) | 3084 (1) | 585 (10) |
| C(4) | −284 (1) | 7580 (2) | 3310 (1) | 554 (10) |
| C(5) | 857 (1) | 5810 (2) | 4064 (1) | 342 (6) |
| C(6) | 1084 (1) | 6512 (2) | 4650 (1) | 449 (8) |
| C(7) | 1599 (1) | 6290 (2) | 4923 (1) | 538 (9) |
| C(8) | 1893 (1) | 5381 (2) | 4612 (1) | 511 (9) |
| C(9) | 1671 (1) | 4693 (2) | 4024 (1) | 454 (8) |
| C(10) | 1153 (1) | 4902 (2) | 3754 (1) | 393 (7) |
| C(11) | −3 (1) | 3709 (2) | 3830 (1) | 396 (7) |
| C(12) | 256 (1) | 3349 (2) | 4488 (1) | 448 (8) |
| C(13) | 288 (1) | 2043 (2) | 4685 (1) | 541 (10) |
| C(14) | 63 (1) | 1106 (2) | 4216 (2) | 592 (11) |
| C(15) | −190 (1) | 1456 (2) | 3568 (2) | 599 (11) |
| C(16) | −232 (1) | 2752 (2) | 3371 (1) | 512 (9) |
| H(3) | −99 (1) | 677 (3) | 285 (1) | 43 (6) |
| H(4) | −37 (1) | 848 (3) | 323 (2) | 64 (8) |
| H(6) | 86 (1) | 707 (2) | 489 (1) | 31 (5) |
| H(7) | 174 (1) | 671 (3) | 538 (1) | 47 (7) |
| H(8) | 227 (1) | 517 (2) | 481 (1) | 38 (6) |
| H(9) | 188 (1) | 405 (2) | 379 (1) | 34 (5) |
| H(10) | 100 (1) | 438 (2) | 332 (1) | 30 (5) |
| H(12) | 43 (1) | 401 (2) | 482 (1) | 26 (5) |
| H(13) | 53 (1) | 188 (3) | 515 (1) | 49 (7) |
| H(14) | 11 (1) | 26 (2) | 436 (1) | 39 (6) |
| H(15) | −37 (1) | 78 (3) | 332 (2) | 62 (8) |
| H(16) | −41 (1) | 306 (3) | 283 (1) | 60 (8) |

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* Lists of structure factors, anisotropic thermal parameters, least-squares planes, dihedral angles and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38112 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

angles are shown in Fig. 1. Further details of the molecular geometry have been deposited. There are no essential geometrical differences between the two independent molecules; almost all the corresponding bond distances and angles are equal within the limits of error. Each molecule has approximate 2 ($C_2$) symmetry, the twofold axes lying on the pyrazine-ring planes and passing perpendicularly through the midpoint of N···N. The two pyrazine rings are approximately planar, maximum displacements of the atoms being 0·033 Å for C(1) of molecule *A* and 0·039 Å for C(3) of molecule *B*. These displacements are, however, significant. C(5) and C(11) of the phenyl rings and also C(1) and C(2) of the pyrazine rings, to which the phenyl rings are bonded, are displaced significantly from the mean plane in opposite directions to avoid short contacts between the *ortho*-substituted phenyl rings. Moreover, this ring repulsion makes C(1)—C(2) longer than C(3)—C(4), as has also been found in 1,2-diphenylbenzene (Aikawa, Maruyama, Ohashi & Sasada, 1978). The mean C—C and C—N bond distances of 1·388 and 1·336 Å in the pyrazine rings show good agreement with those in tetramethylpyrazine (TMP) (Braam, Eshuis & Vos, 1981), TMP.3$H_2O$ (Braam, Eikelenboom, Van Dijk & Vos, 1981) and pyrazine itself (Wheatley, 1957). The mean C—C—N and C—N—C bond angles of 121·2 and 117·5° are also in agreement with those in TMP, TMP.3$H_2O$, and pyrazine.

The mean C—C distance of 1·385 Å in the phenyl rings agrees well with the expected value and the angles within the ring are all normal with an average value of 120·0°. The phenyl rings are planar. The lengths of the C—C bonds joining the phenyl rings to the pyrazine rings range from 1·482 to 1·492 Å, with an average value of 1·487 Å. These values agree well with those in 1,3,5-triphenylbenzene (Lin & Williams, 1975) and in 1,2-diphenylbenzene. They are, however, longer than the values of 1·454 Å in 2,5-diphenylpyrazine (Laing & Sommerville, 1976) and 1·454 Å in 3,6-diphenyl-*s*-tetrazine (Ahmed & Kitaigorodsky, 1972). The two phenyl rings are rotated in the same direction from the pyrazine-ring plane by 51·4 and 40·2° for molecule *A* and 51·0 and 38·0° for molecule *B* because of the steric hindrance between the two phenyl rings. Such ring twists are sufficient to avoid short intramolecular non-bonded contacts; C(5)···C(12), C(10)···C(11) and C(10)···C(12) are 3·167, 3·261 and 3·317 Å for molecule *A*, and 3·129, 3·252 and 3·274 Å for molecule *B*, respectively. These features of the phenyl rings may be compared with those in phenyl-substituted compounds. The dihedral angles between the phenyl planes and the central-ring plane are 62·1 and 42·5° in 1,2-diphenylbenzene, 40·7, 37·2 and 36·1° in 1,3,5-triphenylbenzene, whereas the angles are only 20° in 2,5-diphenylpyrazine, 16 and 25° in *p*-terphenyl (Baudour, Delugeard & Cailleau, 1976).

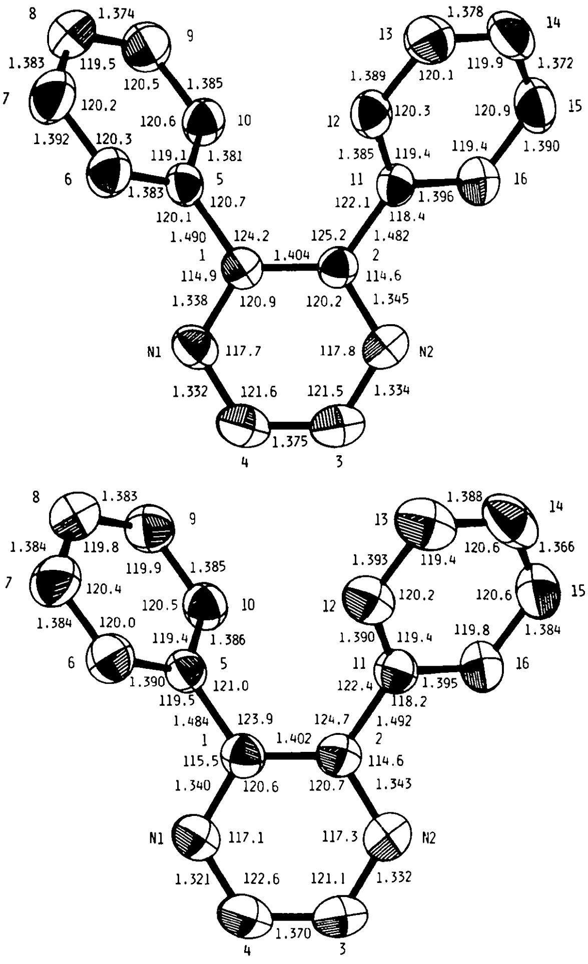

Fig. 1. Molecular structures of molecule *A* (top) and molecule *B* (bottom) projected on the pyrazine-ring planes, with atomic numbering, bond lengths (Å) and bond angles (°). Thermal ellipsoids are drawn at the 50% probability level. The e.s.d's of the bond distances are 0·002–0·003 Å, those of the bond angles 0·2–0·3°.

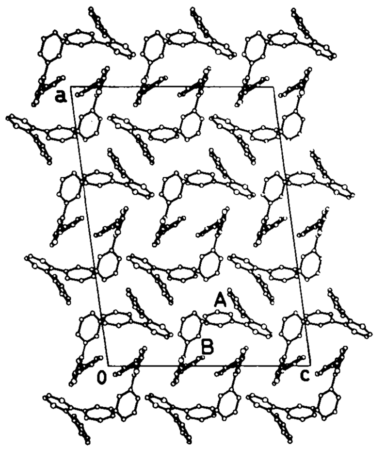

Fig. 2. The crystal packing of molecules *A* and *B* viewed down **b**. *A* and *B* refer to the molecules in Table 1.

The molecular arrangement in the crystal viewed along **b** is illustrated in Fig. 2. The crystal is built up of individual molecules, with adjacent molecules held together by van der Waals forces.

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# 4-Amino-1-phenyl-1,2,5,6-tetrahydrophosphorin-3-carbonitrile, $C_{12}H_{13}N_2P$

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(*Received* 20 *May* 1982; *accepted* 18 *October* 1982)

**Abstract.** $M_r = 216\cdot2$, monoclinic, space group $P2_1/c$, $a = 11\cdot670\,(2)$, $b = 7\cdot794\,(2)$, $c = 12\cdot785\,(8)$ Å, $\beta = 100\cdot37\,(3)^\circ$, $U = 1143\cdot8$ Å$^3$, $Z = 4$, $D_x = 1\cdot26$ Mg m$^{-3}$, $\lambda(\text{Mo } K\alpha) = 0\cdot71073$ Å, $\mu = 0\cdot205$ mm$^{-1}$, $T = 295$ K. Final $R = 0\cdot031$ for 1516 observed reflections. The molecules are hydrogen-bonded in the crystal, forming infinite chains extending along the crystallographic $c$ axis.

**Introduction.** Phosphorinane, a heterocyclic analogue of cyclohexane, has been shown (Lambert & Oliver, 1971) to exist predominantly in the chair form in the liquid state, with the P—H bond disposed axially to the ring.

A number of X-ray structural determinations (McPhail, Breen & Quin, 1971; McPhail, Breen, Somers, Steele & Quin, 1971; McPhail, Luhan, Featherman & Quin, 1972) have demonstrated that this configurational preference persists in the solid state for 1-phenyl- and 1-methyl-substituted phosphorinanes. The considerable steric interactions between the heterocyclic ring and the P substituent are partially relieved, in the case of the phenyl group, by out-of-plane distortion at the phenyl *ipso* C atom. The present study is concerned with an X-ray structural study of a partially dehydrogenated phosphorinane in which, due to heterocyclic-ring flattening, the steric strain should be reduced.

**Experimental.** Crystal *ca* $0\cdot22 \times 0\cdot25 \times 0\cdot44$ mm, Enraf–Nonius CAD-4 diffractometer controlled by a PDP8/a computer, take-off angle 5°, Mo $K\alpha$ radiation filtered by a square-graphite-crystal monochromator, cell dimensions by least-squares refinement of the setting angles of 25 accurately centered reflections; 2005 independent reflections (to $\theta \leq 25^\circ$), $\omega$–$2\theta$ scans, *ZIGZAG* routine (Enraf–Nonius, 1977), background counts taken on each side of the peak, intensities of three standard reflections measured every 8000s, no significant change in intensities, 1516 observed $[I \geq 3\sigma(I)]$, Lp correction; direct methods, automatic multisolution routine of *SHELX* 76 (Sheldrick, 1976) used with all unique reflections to generate a series of $E$ maps, one of which correctly located all non-H atomic positions, full-matrix least-squares refinement with isotropic temperature factors gave $R = 0\cdot122$ for the observed reflections, anisotropic temperature factors

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