

## Structures of Nitrogen-Containing Aromatic Compounds. III. Benzalazine, Redetermination and Refinement

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(Received 6 April 1976; accepted 8 May 1976)

Benzalazine is orthorhombic, *Pbcn*,  $a = 13.08$  (2),  $b = 11.75$  (2),  $c = 7.56$  (1) Å,  $Z = 4$ .  $R = 0.047$  for 733 observed data (diffractometer, monochromated Mo  $K\alpha$ ), all C and N atoms anisotropic, all H's included. N–N = 1.41, N=C = 1.27, C–C = 1.46, mean C–C in the phenyl ring = 1.385 ( $\pm 0.01$ ) Å after correction for thermal motion. A discussion is given of the relation between the bond lengths and bond orders of C–C, C–N and N–N bonds. The criteria necessary for  $\pi$ -electron delocalization in N-containing organic compounds are described.

### Introduction

The structure of benzalazine was originally solved by projection down two axes (Sinha, 1970). The bond lengths were relatively inaccurate (e.s.d.'s of about 0.02 Å) and those of interest, *i.e.* N–N, N=C and C–C(ph), differed greatly from the results found in the closely related compound salicylaldehyde azine (Arcovito, Bonamico, Domenicano & Vaciano, 1969). The structure of benzalazine has therefore been redetermined to obtain more precise values.

### Experimental

Suitable crystals were obtained from a chloroform/ethanol solution. Cell dimensions (Table 1) were obtained by least-squares refinement of  $2\theta$ ,  $\chi$  and  $\phi$  angles for 25 reflexions measured on a Philips four-circle diffractometer. Intensities were measured for a crystal  $0.3 \times 0.3 \times 0.7$  mm with graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.7107$  Å) for  $\theta$  between 3 and 25°. The  $\omega$ - $2\theta$  scan mode was used: the scan width was 1.2°, the scan time was 30 s, and the background was counted for 30 s for each reflexion. Three reflexions were used as standards and remeasured after every 60 reflexions; no crystal decomposition was detectable. Of the 1213 reflexions measured (including space-group extinctions) 733 were classed as observed, *i.e.*  $I > 1.65\sigma(I)$ . Only Lorentz-polarization corrections were applied.

Table 1. Crystal data

$C_{14}N_2H_{12}$	Orthorhombic, <i>Pbcn</i>
$a = 13.08$ (2) Å	$V = 1162$ Å <sup>3</sup>
$b = 11.75$ (2)	$Z = 4$
$c = 7.56$ (1)	$D_m = 1.18$ g cm <sup>-3</sup>

The coordinates reported by Sinha (1970) were used as the starting parameters and the structure was refined by block-diagonal least squares, first isotropically, then with the N and C atoms anisotropic. At conver-

gence,  $R = 0.047$  for 733 observed data.\* Four reflexions, 002, 121, 200 and 020, were suffering badly from extinction and were omitted from the refinement. Weights were proportional to  $1/\sigma(F)$ ; the scattering factors were for neutral atoms, taken from *International Tables for X-ray Crystallography* (1962).

The atomic coordinates and thermal parameters are given in Table 2, with the estimated standard deviations in parentheses. Table 3 lists bond lengths and angles (uncorrected for thermal motion) and compares these with the analogous values reported by Sinha (1970) and Arcovito *et al.* (1969). Fig. 1 shows the numbering system and some bond lengths and angles after correction for thermal motion (Cruickshank, 1956).

### Discussion

#### Molecular structure

The results confirm the general correctness of the structure reported by Sinha (1970). The precision of the parameters is now much improved; the planarity of the phenyl ring is very good while C(1) is significantly out of the plane (Table 4). Table 3 shows that all C–C distances in the phenyl ring are far shorter than the accepted value of 1.395 Å; nevertheless there is high internal consistency in the new results (Table 3). This foreshortening, which increases systematically with distance from C(1), is caused by the thermal motion of the ring. Application of corrections based on the simple 'rigid body' approximation proves to be inadequate and cannot produce a lengthening of the C–C bonds to 1.39 Å. For this reason, the true accuracy of the bond lengths is lower than the precision deduced from the least-squares analysis, and the bond lengths in Fig. 1 have a probable error of about 0.01 Å.

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31885 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

## Correlation between bond lengths and bond orders

Much has been written about the relation between the lengths of C-C bonds and their bond orders, starting with the pioneering work of Pauling (1960) and continuing to the present (Sim & Sutton, 1973).

Table 2. Fractional atomic coordinates and thermal parameters

Atomic coordinates ( $\times 10^4$  for N, C;  $\times 10^3$  for H) and isotropic thermal parameters.

	x	y	z	$B_{iso}(\text{\AA}^2)$
N	526 (1)	18 (1)	212 (2)	—
C(1)	974 (1)	877 (1)	-446 (2)	—
C(2)	2063 (1)	1081 (1)	-195 (2)	—
C(3)	2501 (1)	2051 (1)	-920 (2)	—
C(4)	3535 (1)	2255 (1)	-729 (2)	—
C(5)	4136 (1)	1497 (1)	179 (2)	—
C(6)	3708 (1)	541 (1)	907 (2)	—
C(7)	2679 (1)	327 (1)	721 (2)	—
H(1)	55 (1)	145 (1)	-117 (2)	4.0 (4)
H(3)	205 (1)	259 (1)	-156 (2)	3.6 (4)
H(4)	384 (1)	294 (1)	-130 (2)	5.1 (4)
H(5)	489 (1)	165 (1)	29 (2)	4.1 (4)
H(6)	414 (1)	-2 (1)	157 (2)	4.4 (4)
H(7)	238 (1)	-37 (1)	122 (2)	3.6 (4)

Anisotropic thermal parameters ( $\times 10^4$ ). The form of the expression is  $\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$ .

	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
N	68 (1)	99 (1)	235 (3)	17 (2)	-4 (3)	15 (4)
C(1)	76 (1)	74 (1)	187 (4)	19 (2)	-9 (3)	-6 (4)
C(2)	66 (1)	72 (1)	159 (3)	16 (2)	-11 (3)	-24 (4)
C(3)	91 (1)	74 (1)	232 (4)	3 (2)	-37 (4)	-4 (4)
C(4)	99 (1)	88 (2)	299 (5)	-42 (2)	1 (4)	-17 (5)
C(5)	75 (1)	113 (2)	317 (5)	-16 (2)	-16 (4)	-62 (6)
C(6)	75 (1)	108 (2)	268 (4)	31 (2)	-39 (4)	-11 (5)
C(7)	75 (1)	86 (2)	196 (4)	17 (2)	4 (3)	8 (4)

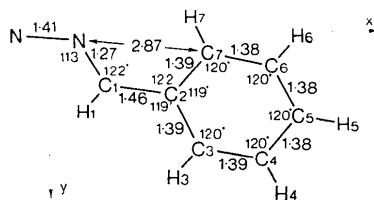


Fig. 1. A projection of the asymmetric unit down  $c$  showing the numbering system, bond lengths ( $\text{\AA}$ ) and bond angles ( $^\circ$ ) after correction for thermal motion.

Table 4. Least-squares plane defined by the phenyl ring

Direction cosines of the normal to the plane			
Referred to	$a$	$b$	$c$
	-0.179	0.499	0.848
Deviations from the plane ( $\text{\AA}$ )			
C(2)	C(3)	C(4)	C(5)
-0.001	0.001	0.001	-0.003
C(6)	C(7)	N	C(1)
0.003	-0.001	-0.005	-0.027

Bernstein (1961) describes very clearly the need to compare only bonds between atoms which have identical hybridization because a 'single' bond will have a different length not only for ( $sp^3$ )C-C( $sp^3$ ), ( $sp^2$ )C-C( $sp^2$ ) and ( $sp$ )C-C( $sp$ ) but also for all other possible combinations (Fig. 2). These difficulties become worse for C-N and N-N bonds because the state of hybridization of the N atom is not always clearly defined. For a N atom involved in a double bond,  $sp^2$  hybridization is indicated; yet the bond angle is not necessarily close to  $120^\circ$  and values between  $110$  and  $115^\circ$  are regularly observed. The vinylideneamines appear to contradict this generality because three structures have been reported with large C=N-C angles:  $180^\circ$  (Wheatley, 1954),  $171^\circ$  (Bullough & Wheatley, 1957) and  $144^\circ$  (Daly, 1961). However, two others have C=N-C angles of  $125$  and  $123^\circ$  (Naqvi & Wheatley, 1970) and similar values have been observed in diimides:  $127$ ,  $128^\circ$  (Vincent & Wheatley, 1972a) and  $134$ ,  $130^\circ$  (Vincent & Wheatley, 1972b). When a N atom is  $\sigma$ -bonded to three other atoms by single bonds, the bond angles can lie anywhere in the range  $105$  to  $125^\circ$ , and the difficulty is to make the possibly arbitrary choice between assigning  $sp^2$  or  $sp^3$  hybridization to the N atom (Orville-Thomas, 1966). This problem has been reviewed in some detail (Stals, 1970) but is not yet fully resolved.

What is offered here is a simple-minded approach based on a subjective choice of bond lengths of C-N and N-N bonds which have well defined valence bond orders of 1, 1.5 and 2 between pairs of atoms which have  $sp^2$  hybridization. These values have then been used to construct the curves relating bond length to bond order. The curves were neither expected to be

Table 3. Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ )

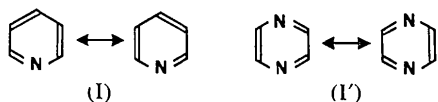
These values are not corrected for thermal motion. The e.s.d.'s are about  $0.005 \text{\AA}$ , except for N-N' for which the value is doubled.

	(1)	(2)		(1)	(2)
N—N'	1.412	1.380	N'—N—C(1)	112.6	115.0
N—C(1)	1.270	1.264	N—C(1)—C(2)	122.1	122.5
C(1)—C(2)	1.456	1.465	C(1)—C(2)—C(3)	119.2	119.0
C(2)—C(3)	1.388	1.390	C(1)—C(2)—C(7)	122.0	122.0
C(3)—C(4)	1.382	1.383	C(3)—C(2)—C(7)	118.7	118.6
C(4)—C(5)	1.372	1.402	C(2)—C(3)—C(4)	120.4	121.2
C(5)—C(6)	1.372	1.365	C(3)—C(4)—C(5)	120.0	120.0
C(6)—C(7)	1.375	1.390	C(4)—C(5)—C(6)	119.9	118.8
C(7)—C(2)	1.384	1.385	C(5)—C(6)—C(7)	120.5	122.0
			C(6)—C(7)—C(2)	120.3	119.6

References: (1) Sinha (1970). (2) Arcovito, Bonamico, Domenicano & Vaciago (1969).

linear nor to be parallel to the analogous curve for C-C bonds.

The choice of suitable reference compounds presents difficulties because it is not always clear what the true bond order is. In valence bond terms (Pauling, 1960), an order of 1.5 can be assigned to the C-N and C-C bonds in both pyridine (I) and pyrazine (I') because, in each case, the two contributing structures have identical energies.



The same approach can be used for the N-N bond; but in pyridazine (II) (Evans & Wiselogle, 1945) the two structures cannot have identical energies and therefore will not contribute equally to the hybrid structure. Thus the N-N bond certainly will not have a bond order of 1.5 and neither will the C-N nor C-C bonds. Tetrazine (III) does have two contributing forms of equal energy, and therefore the N-N bond in this compound can legitimately be assigned a bond order of 1.5.

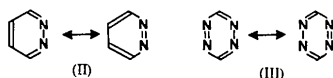


Table 5 lists the compounds and the bond lengths and bond orders which were chosen as the standards, and the resulting curves are shown in Fig. 3. All bond lengths are given to 0.01 Å because their innate error is probably of this magnitude: in most cases the structures have been determined at room temperature and the r.m.s. amplitudes of vibration of the atoms lay between 0.1 and 0.2 Å.

Table 5. Bond lengths (Å) and bond orders for bonds between C and N atoms in which both atoms are assumed to have  $sp^2$  hybridization

Bond type	Bond order*		
	1.0	1.5	2.0
C-C	1.48 <sup>a</sup>	1.39 <sup>a</sup>	1.34 <sup>a</sup>
C-N	1.45 <sup>c</sup>	1.34 <sup>a</sup>	1.27 <sup>b</sup>
N-N	1.41 <sup>b</sup>	1.31 <sup>d</sup>	1.23 <sup>c</sup>

\* This corresponds to  $1+P$ , where  $P$  is the double-bond character, as defined by Bernstein (1961) and Pauling (1960). References: (a) Butadiene, benzene, ethylene, pyridine, s-triazine; Orville-Thomas (1966), Daudel, Lefebvre & Moser (1959), Streitweiser (1961), Cruickshank & Sparks (1960), Lancaster & Stoicheff (1956), Wheatley (1955). (b) Salicylaldehyde azine; Arcovito *et al.* (1969). See also Lofthus (1959). (c) 4-Phenylazoazobenzene; Gilardi & Karle (1972). (d) 3,6-Diphenyl-*s*-tetrazine; Ahmed & Kitaigorodsky (1972).

The curves in Fig. 3 are not parallel: that for N-N bonds is closest to linearity. Sabesan & Venkatesan (1971) assumed that an exactly linear relation existed between bond length and bond order for N-N bonds to obtain the necessary correlation from their Hückel

MO calculations. From these calculations they derived values of 1.26 for N=N and 1.46 Å for N-N, which are significantly larger than the values used here to define the curve.

The bond lengths in both 2,5-diphenylpyrazine (Laing & Sommerville, 1976) and benzalazine fit well with the predictions from Fig. 3. The pyrazine ring is completely aromatic in the sense that the derived C-C and C-N bond orders are 1.5.

Of more interest are the bond orders that can be deduced for the N-N, N-C and C-C bonds in other compounds with accurately known crystal structures. A list is given in Table 6 and their structural formulae are illustrated in Fig. 4. The range of compounds was limited to those in which the C and N atoms were linked by alternating single and double bonds, formed part of a planar cyclic system or, in the open chain cases, were  $sp^2$  hybridized (as indicated by the bond angles).

Comparisons of the N-N, N-C and C-C bonds in (IV), (V) and (VI) show that the bonding in these compounds is similar: N-N 1.373; 1.382; 1.372 Å; C-N

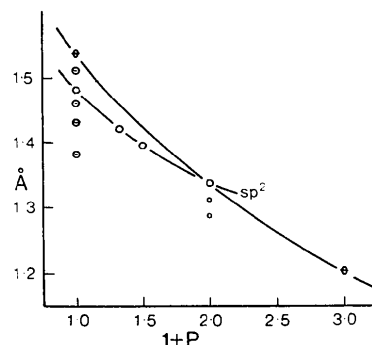


Fig. 2. Dependence of bond lengths (Å) on bond order ( $1+P$ ) for C-C bonds: data from Bernstein (1961) and Orville-Thomas (1966). The curve labelled  $sp^2$  is for pairs of C atoms both of which have  $sp^2$  hybridization. The other curve joins the values of the bond lengths found in ethane, ethylene and acetylene and corresponds to the earliest proposal of Pauling.

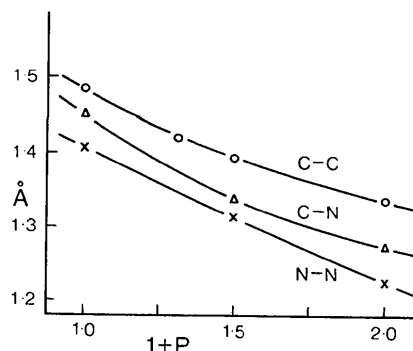


Fig. 3. Relation between bond length (Å) and bond order ( $1+P$ ) for C-C, C-N and N-N bonds in which both atoms are assumed to have  $sp^2$  hybridization: data from Table 5.

1.297, 1.291; 1.310, 1.314; 1.295, 1.307 Å; C–C (fusion) 1.379; 1.388; 1.380 Å. It is also evident that there is delocalization of the electrons as the approximate bond orders are N–N 1.15, C–N 1.75: the sum of the bond orders for both the N atoms is close to 3 (Lindner, Manne & Mårtensson, 1966).

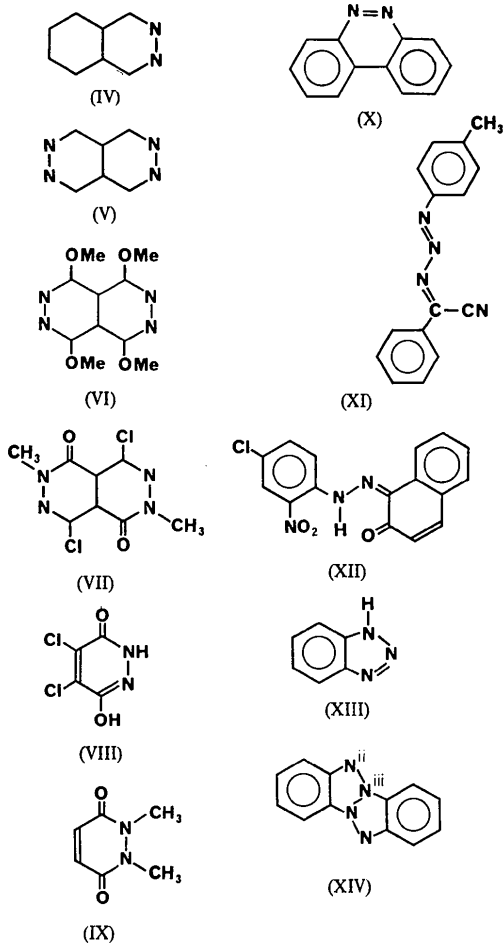


Fig. 4. Structural formulae of the molecules listed in Table 6 and referred to in the text. For compounds (IV) to (VII) and (XIV) no attempt has been made to assign a unique valence-bond formulation. The others have been represented by their principal canonical forms.

Table 6. Nitrogen-containing compounds which are either cyclic, planar or aromatic

	Number in Fig. 4	Reference
2,3-Diazanaphthalene	(IV)	Huiszoon, van de Waal, van Egmond & Harkema (1972)
Pyridazino[4,5-d]pyridazine	(V)	Sabelli, Tangocci & Zanazzi (1969)
1,4,5,8-Tetramethoxypyridazino[4,5-d]pyridazine	(VI)	Fanfani, Zanazzi & Sabelli (1972)
2,6-Dimethyl-4,8-dichloro-2H,6H-pyridazino[4,5-d]pyridazine-1,5-dione	(VII)	Sabelli & Zanazzi (1972)
4,5-Dichloro-3,6-pyridazinedione	(VIII)	Otterson (1973a)
1,2-Dimethyl-3,6-pyridazinedione	(IX)	Otterson (1973b)
9,10-Diazaphenanthrene	(X)	van der Meer (1972)
1-p-Tolyl-3-( $\alpha$ -cyano)benzylidene-triazene	(XI)	Schilling & Nordman (1972)
1,2-Naphthoquinone-1-(2-nitro-4-chlorophenyl)hydrazone	(XII)	Guggenberger & Teufer (1975)
Benzotriazole	(XIII)	Escande, Galigné & Lapasset (1974)
Dibenzo-1,3a,4,6a-tetraazapentalene	(XIV)	Laing (1976)

The situation in (VII), (VIII) and (IX) is quite different (Table 7). The bond orders for the N–N and C–N bonds (Fig. 3) show that there is delocalization in all cases, but in (IX) the N–C bonds approach aromatic character. The sum of the bond orders for the N atom bonded to only *two* other atoms is close to 3 in (VII) and (VIII), but for a N atom bonded to *three* atoms the sum of the bond orders (taking N–H or N–CH<sub>3</sub> as BO = 1.0) is well above 3, between 3.4 and 3.7. Thus, the pair of *p*-electrons on the N atom involved in three  $\sigma$ -bonds is delocalized into the ring. This is not true for a N atom bonded to two atoms by one formal single and one formal double bond. In this case, the lone pair is not involved in the delocalization and is basic.

Table 7. Bond lengths (Å)

The validity of the bond lengths in (VIII) is difficult to assess for several reasons: there are two molecules in the asymmetric unit with differences in length for chemically identical bonds of about 0.01 Å (columns VIIIa and VIIIb), yet the e.s.d.'s are about 0.004 Å; also the bond lengths derived from the refinement of 1341 low-angle data with  $\sin \theta/\lambda < 0.71$  differ by as much as 0.02 Å from the results obtained from the refinement of 1317 high-angle data,  $\sin \theta/\lambda > 0.61$ .

	(VII)	(VIIIa)	(VIIIb)	(IX)
N–N	1.359	1.363	1.374	1.399
C–N	1.299	1.296	1.278	1.367*
C–N(R)	1.379	1.335	1.344	1.358*

\* These are chemically identical bonds.

In (X) N–N is 1.292 and the C–N lengths are 1.392, 1.401 Å. The C–C lengths alternate between 1.37 and 1.42 Å in the phenyl rings; the longest C–C bond, 1.436 Å, links the two six-membered rings. The N–N bond order is about 1.60 while C–N has a bond order of 1.25, showing that while there is electron delocalization in the molecule the heterocyclic system is 'less aromatic' than (IV). Van der Meer (1972) showed that the 'degree of aromaticity' in (X) is close to that in phenanthrene.

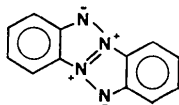
(XI) and (XII) are open-chain compounds, but the bonding within the chains differs. The bond lengths in (XI) show that there is almost no delocalization in the chain: N–N 1.403, N=N 1.239, C=N 1.315, N–C(ph)

1.414, (ph)C–C(*sp*<sup>2</sup>) 1.469 Å (e.s.d.'s between 0.01 and 0.02 Å). The angle N–N=N is 109.5°.

On the other hand, (XII) shows very marked electron delocalization in the C–N–N–C chain: C–N(H) 1.394, (H)N–N 1.333, N=C 1.312 Å. Guggenberger & Teufer (1975) discussed the bonding and concluded that the hydrazone formulation, (XII), is the best approximation and that their results eliminated the alternative azophenol type of structure. Not only is the O=C–C=N arrangement favoured over the HO–C=C–N structure but the strong intramolecular hydrogen bond between N–H and O=C aids in delocalizing the electron density in the system. Once again, the sum of the bond orders is close to 3 for the N atom bonded to only two atoms, but the value is close to 3.6 for N(H).

Benzotriazole, (XIII), is unique in having four molecules per asymmetric unit (Escande, Galigné & Lapasset, 1974) and thus gives an ideal opportunity for checking the internal consistency in a crystal structure. Unfortunately, the combination of high thermal motion and poor definition of the H atoms has produced a lower precision than expected (e.s.d.'s about 0.01 Å; the largest difference in length between pairs of chemically identical bonds is 0.03 Å). The mean values are C–N(H) 1.364, (H)N–N 1.346, N–N 1.310, N–C 1.377 Å (with a probable error of at least 0.01 Å). The bond orders deduced from these values show that there is significant delocalization of the electrons in the triazole ring. The sums of the bond orders for the N atoms are close to 3 for both of those formally double-bonded but the sum is about 3.65 for N(H) – the same effect that was found in (VII), (VIII), (IX) and (XII).

Comparison of (XIII) and (XIV) shows that there is a remarkable similarity between the lengths of both the C–N bonds and the analogous C–C bonds in the phenyl rings: the same pair of C–C bonds is significantly shorter than all the others (Laing, 1976). (XIV) perhaps represents the ultimate in delocalization in this group of compounds because it is impossible to draw even a Kekulé-type valence-bond structure for this molecule. The sums of the bond orders for the two N atoms reflect the large charge transfer that takes place: for N(II) the sum is 2.6, while for N(III) it is 3.7, values which are consistent with the net charges of –0.33 and +0.38, derived from HMO calculations (Burke-Laing, Sparks, Laing & Trueblood, 1976; Chia & Simmons, 1967; Paoloni, Gramaccioni & Vaciago, 1966). Thus (XIV) could be written as (a), a canonical form which must be a major contributor to the hybrid structure of (XIV) in the ground state, contrary to Pauling's (1960) adjacent-charge rule.



(a)

From the results for compounds (IV) to (XIV) it is evident that a molecule containing a formal N–N single or double bond in a conjugated system will show electron delocalization if one N atom is involved in three  $\sigma$ -bonds, especially if a N–H group is present, because either intra- or intermolecular hydrogen bonding can facilitate the delocalization, or if a C=O group is adjacent to one of the N atoms.

A survey of several other compounds confirms these observations. In diphenylformazan (XVIII) (Omel'chenko, Kondrashev, Ginzburg & Neigauz, 1973) the N–N and N–C bonds show that there is delocalization in the N–N–C–N–N chain. Once again, hydrogen bonding is involved in the stabilization of the system because the molecules of diphenylformazan are linked by intermolecular hydrogen bonds to form infinite chains parallel to **b**. Although the precision is low, the same pattern is present, *i.e.* the sum of bond orders for N(H) far exceeds those of the other three N atoms. The N–N and N–C bonds remain almost unchanged in length when diphenylformazan acts as a N-donor chelating ligand in [Cu<sup>I</sup> bis(diphenylformazan)]<sup>+</sup>, emphasizing that the  $\sigma$ -donor pairs play little part in the bonding in the N–N–C–N–N chain (Balt, Renkema, van Capelleveen & Stam, 1976).

Diazoaminobenzene (XVII) exists in two polymorphic forms (Gladkova & Kondrashev, 1972). In both, (ph)C–N is short, about 1.43 Å, and the N–N lengths, which cannot be clearly differentiated, are close to 1.30 Å. The molecules are hydrogen-bonded in spirals parallel to **b**, and the electrons in the N–N–N chain are evidently delocalized (mean N–N bond order of 1.5). Again, the presence of a N(H) group and intermolecular hydrogen bonding seems to aid in the delocalization of the  $\pi$ -electrons.

By contrast, both 2,2'-dibromo-4,4'-bis(*p*-methoxybenzylideneamino)biphenyl (XV) (Lesser, de Vries, Reed & Brown, 1975) and  $\alpha,\alpha'$ -azobis(4-bromobenzaldehyde)bis(*O*-carboxyoxime) diethyl ester (XVI) (Go & Kartha, 1975) have well defined single and double bonds between the N and C atoms in their chains: all N atoms in both compounds are bonded to only two other atoms. In (XV) the mean values of the bonds are N=C 1.27, C–N 1.42 Å; in (XVI) they are N=N 1.22, C=N 1.27 and C–N 1.48 ( $\pm 0.02$ ) Å. The bonding in the allene-like systems in the vinylideneamines and diimides does not fall within the scope of the conclusions made above because the near linearity of the C=C=N and N=C=N groups implies that the central C atom would be classed as *sp* hybridized.

The remarks made above apply to the purine bases and compounds related to them. The bond lengths in purine (Watson, Sweet & Marsh, 1965) show that the six-membered ring is an aromatic system while the bonding in the five-membered ring is very like that in benzotriazole (XIII). Xanthazole (Mez & Donohue, 1969), 8-azaguanine (Sletten, Sletten & Jensen, 1968) and benzimidazole (Dik-Edixhoven, Schenk & van der Meer, 1973) show significant electron delocalization;

once again, the N atoms involved in three  $\sigma$ -bonds have the sum of their bond orders exceeding 3.5. When two possible tautomeric forms can exist, the difference in energy is often very small, and in isocytosine (Sharma & McConnell, 1965) both forms are found in the crystal. Thus the lone pair on the N atom bonded to two other atoms can attract protons strongly, while the N(H) group with its high sum of bond orders can readily donate its H atom to form strong hydrogen bonds (Marsh, 1968).

The bonding in sydnones (Baker & Ollis, 1957; Albert, 1959) poses the same problems as does that in (XIV) – no simple valence bond structure can be drawn. The five-membered ring is aromatic in character, and the bonding of the N atoms has the characteristics common to the systems (V) to (XIV) where electron delocalization is large. Crystal structures of 3,3'-ethylenebis-sydnone and its 4,4'-dichloro derivative (Hope & Thiessen, 1969) and *N*-(*p*-bromophenyl)-sydnone (Bärnighausen, Jellinek, Munnik & Vos, 1963) show that the C–C bond is aromatic, and that the sum of the bond orders of the N atom bonded to three atoms is 4, *i.e.* its pair of *p*-electrons is completely delocalized into the ring. In 1,2,4-triazole (Goldstein, Ladell & Abowitz, 1969) each of the C–N bonds has a bond order close to 1.5, but the sums of the bond orders of the two N atoms in the N–N bond differ by nearly one unit. In tetrazolo[1,5-*b*]benzothiazole (Domiano & Musatti, 1974) the four N atoms in the tetrazole ring show  $\pi$ -delocalization but have only partly aromatic character. Each of the three N atoms bonded to only two other atoms has a sum of bond orders significantly less than 3; but the N atom at the fusion has a sum of bond orders of 3.8. Work by Seccombe & Kennard (1973) and Seccombe, Tillack & Kennard (1973) on a series of cyclic triazoles shows that the comments made above also apply to these compounds. Although they include cationic and anionic species as well as neutral molecules, all have at least one N of the cyclic system bonded to either a H, N or C atom with the resulting delocalization of the  $\pi$ -electrons.

The structures of a series of compounds related to tetraphenylhydrazine, determined at  $-160^\circ\text{C}$ , illustrate the effects of steric strains on bond lengths. In *N*-(diphenylmethylene)aniline (Tucker, Hoekstra, ten Cate & Vos, 1975) bond lengths are C=N 1.287, (ph)C–N 1.420, (ph)C–C(N) 1.490, 1.493 Å. Tetraphenylhydrazine has two independent molecules per asymmetric unit (Hoekstra, Vos, Braun & Hornstra, 1975), with bond lengths N–N 1.407, 1.404; C–N 1.427, 1.416, 1.419, 1.424, 1.425, 1.416 Å. In diphenylamino-triphenylmethane (Hoekstra & Vos, 1975), (ph)C–N 1.405, 1.438; ( $sp^3$ )C–N 1.500 Å; while in tetraphenylethylene, the (ph)C–C( $sp^2$ ) lengths are 1.491, 1.492, 1.496, 1.503 Å and C=C is 1.356 Å. In general, the N–N, N–C and N=C are close to the values chosen as standards (Table 5), the largest difference being for the C–N single bond.

There are many apparently single N–C bonds whose

lengths are close to 1.42 Å, usually where the C atom is in a phenyl ring. It is possible, therefore, that this shortening is due to a small delocalization. In tricycloquinazoline (Iball & Motherwell, 1969), the mean lengths were central( $sp^2$ )N–C( $sp^2$ ) 1.425, (outer)N–C(ph) 1.397, (outer)N–C( $sp^2$ ) 1.279 Å. The sum of the bond orders (Fig. 3) for the outer N is almost exactly 3, and the sum for the central N is about 3.3. The structure of azobenzene is, unfortunately for this comparison, disordered (Brown, 1966) but the (ph)C–N bonds in several related compounds are short: 1.42, 1.43 Å in 4,4'-azodiphenetole (Galigné, 1970); 1.43 Å in bisphenylazostilbene (Chesick, 1973); 1.42 Å in *trans*-2,2'-azo-*p*-cymene (Wetherington, Holmes & Moncrief, 1974); 1.426, 1.430, 1.438 Å in the two crystalline forms of hexanitroazobenzene (Graeber & Morosin, 1974); 1.443 Å in *trans-p,p'*-dichloroazobenzene (Hope & Victor, 1969). The N=N length in these compounds lies between 1.243 and 1.255 Å. The effect on the (ph)C–N, N=C(H) and (H)C–C(ph) bonds in benzyldeneanilines, caused by change in substituents on the phenyl rings, has been discussed by Bürgi & Dunitz (1969, 1970). They concluded that electrons in the C=N group were delocalized and interacted with the  $\pi$ -clouds of the phenyl rings.

The above compounds also point to the bond length that remains a problem: the single bond between two  $sp^2$  hybridized C atoms. Can a unique value be assigned to this bond length? Observed values range from 1.45 to 1.51 Å (all with e.s.d.'s of less than 0.01 Å). In (XV), (ph)C–C( $sp^2$ ) lengths were 1.478, 1.470 Å, while (ph)C–C(ph) was 1.489 Å. In (XVI) (ph)C–C( $sp^2$ ) lengths were 1.47, 1.48 Å. In 3,6-diphenyl-*s*-tetrazine, (ph)C–C(tetraz) was 1.454 Å, a value close to those found in benzalazine and salicylaldehyde azine (Table 3). In 2,5-diphenylpyrazine (Laing & Somerville, 1976) the value is 1.475 Å. Values of 1.471 and 1.474 Å were found for (ph)C–C( $sp^2$ ) in *trans*-stilbene (Hoekstra, Meertens & Vos, 1975). Longer lengths have been found in amides: 1.513 Å in  $\beta$ -pyrazine-carboxamide (Rø & Sørum, 1972), 1.501 Å in 6-amido-3-pyridazone (Cucka, 1963). In pyrazinic acid the length is 1.495 Å (Takusagawa, Higuchi, Shimada, Tamura & Sasada, 1974).

In anisaldehyde azine (Galigné & Falgueirettes, 1968), lengths were (ph)C–C(H) 1.510, 1.480; (H)C=N 1.265, 1.300; N–N 1.410 Å. In *s*-triphenyltriazine (Damiani, Giglio & Ripamonti, 1965) there are six chemically identical C–N bonds of order 1.5 whose bond lengths range from 1.321 to 1.359 Å, eighteen aromatic C–C bonds whose lengths range from 1.368 to 1.415 Å and three (ph)C–C( $sp^2$ ) bonds: 1.465, 1.474, 1.485 Å. It is evident that the probable error in all these bond lengths is between 0.01 and 0.02 Å and there is no clear case for choosing any one of the C–C bonds as being more accurate than any other.

Ibata, Shimanouchi, Sasada & Hata (1975) deduced two possible values: 1.498 (for bond index  $p' = 1.0$ ) and 1.520 Å (for bond order  $p = 0$ ) which are close to 1.504

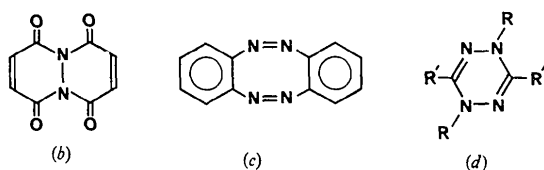
Å, the choice of Pauling (1960). Bond-angle strains can also induce changes in bond length, *e.g.* in biphenylene (ph)C–C(ph) is 1.514 Å while in the six-membered rings the bond lengths alternate in length between 1.37 and 1.42 Å (Fawcett & Trotter, 1966). The effect of non-bonded interactions on bond lengths has been discussed in detail by Bartell (1960).

A 'best' value for ( $sp^2$ )C–C( $sp^2$ ) seems to lie between the 1.470 in *trans*-stilbene and 1.495 Å in tetraphenylethylene. However, the innate inaccuracies in bond lengths deduced from a crystal structure analysis can be far larger than either the estimated standard deviations or the differences which are of interest. A final example which illustrates this is *p,p'*-bitolyl (Casalone, Mariani, Mugnoli & Simonetta, 1969) where there are two independent molecules per asymmetric unit. The (ph)C–C(ph) lengths were 1.459 and 1.486 Å – a difference of  $3\sigma$ ; however, the C–C lengths in the phenyl rings range from 1.361 to 1.403 Å. There is no obvious reason for discrepancies of this size, yet they are commonly observed, *e.g.* in 2-mercaptobenzothiazole (Chesick & Donohue, 1971), and have been discussed by Hughes (1968). The problems involved in attaining accuracy as well as precision in crystal structure determinations have been reviewed in detail (Lide & Paul, 1974). The situation is most succinctly summarized by Kitaigorodsky (1973): 'there seems to be no experiment that can claim an accuracy of above 0.01 Å'.

### Conclusion

A system containing alternating single and double bonds between  $sp^2$ -hybridized C and N atoms can be accurately represented by one simple valence bond structure if all N atoms are bonded to only two other atoms, N or C. If two exactly equivalent structures can be drawn, then the  $\pi$ -electrons in the structure will be aromatic (typically for the cyclic systems); if the structures are not equivalent in energy, only partial delocalization will occur. If a N atom in the system, cyclic or open chain, is bonded to three atoms, its  $p$ -electrons are delocalized into the  $\pi$ -cloud with a resultant increase in aromaticity and the sum of the bond orders of that N atom will be 3.5 or possibly greater. The presence of C=O adjacent to or conjugated with the N atom involved in three  $\sigma$ -bonds will enhance the aromaticity. If the third atom bonded to the N is H, the hydrogen bonding which can result will also enhance the electron delocalization. The lone pair on a N atom bonded to only two other atoms (N or C) is basic and can be involved in the hydrogen bonding. See Fig. 5.

Thus one can understand why the 9,10-diazanaphthalene system should be stable and aromatic as the 1,4,5,8-tetraketo derivative (*b*) [Kealy, 1962; Sasaki, Kanematsu & Ochiai, 1972; *cf.* also 8b,8c-diazacyclopent[*f,g*]acenaphthylene (Atwood, Hrcir, Wong & Paudler, 1974)] although the parent compound pyridazino[1,2-*a*]pyridazine has yet to be isolated.



It is also evident that the diazo analogue of DBTAP (*c*) (Laing, 1976; Carboni, Kauer, Castle & Simmons, 1967) should be isolable, but will have normal N=N bonds and be non-planar, with an eight-membered ring similar to that in cyclooctatetraene. The *N,N*-disubstituted derivatives of *s*-tetrazine (*d*) (Geldard & Lions, 1965) should also show delocalization. Probable bond lengths would be N–N at least 1.41 Å, N=C between 1.27 and 1.30 Å, and N–C at least 1.37 but less than 1.45 Å. The C–N single bond could be longer if the system became non-planar because the N atom could then become  $sp^3$  hybridized with a reduction of delocalization. Recent work by Caira, Giles, Nassimbeni, Sheldrick & Hazell (1976) supports this conjecture. They found in the 1,4-dihydro-tetrazine ring the bond lengths: N–N 1.42, 1.43; C–N 1.40, 1.40; C=N 1.29, 1.28 Å. The delocalization is thus small. However, the ring is clearly boat-like in conformation; the N atoms carrying the H atoms form the bow and stern and are involved in strong hydrogen bonds to the N atoms of adjacent pyridine rings.

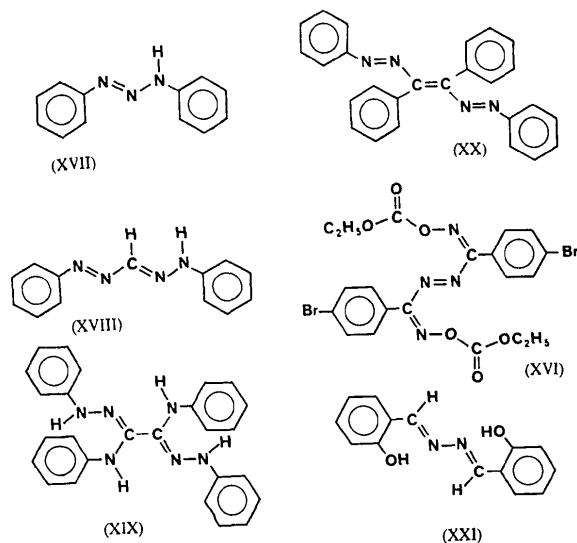


Fig. 5. Some compounds containing chains of alternating single and double C–C, C–N and N–N bonds. (XVII), (XVIII) and (XIX) show marked delocalization of  $\pi$ -electrons in the chain: all have a H atom bonded to one N atom. (XX), (XVI) and (XXI) show little or no delocalization of the  $\pi$ -electrons in the chain. These examples should be compared with (XI) and (XII) in Fig. 4. References: (XVI) Go & Kartha (1975); (XVII) Gladkova & Kondrashev (1972); (XVIII) Omel'chenko, Kondrashev, Ginzburg & Neigauz (1973); (XIX) Harlow & Simonsen (1975); (XX) Chesick (1973); (XXI) Arcovito, Bonamico, Domenicano & Vacigo (1969).

It is a pleasure to thank the South African Council for Scientific and Industrial Research for generous financial assistance; Dr G. Gafner, National Physical Research Laboratory, CSIR for the collection of the intensities; Mrs Polly Sommerville for assistance in the laboratory; and Mr H. A. Candy for preparing the compound.

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## The Crystal Structure of Trisguanidinium Hydrogen Pyrophosphate

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(Received 14 May 1976; accepted 18 June 1976)

The structure of  $[\text{C}(\text{NH}_2)_3]_3\text{HP}_2\text{O}_7$  has been determined from microdensitometer data. The space group is  $P2_12_12_1$  with  $a=9.29$  (2),  $b=17.01$  (2),  $c=9.47$  (2) Å,  $Z=4$ . The guanidinium C–N bonds are all within  $3\sigma$  of the usual 1.33 Å. The P–O–P bridge is symmetrical with P–O bonds of 1.62 Å; the angle is  $128.2$  (4)°. The remaining P–O lengths vary from 1.478 (8) to 1.550 (7) Å. There is a short O–H···O hydrogen bond [2.47 (1) Å] linking pyrophosphate groups into infinite chains. Eighteen of the nineteen H atoms in each formula unit are involved in the hydrogen bonding.

### Introduction

The structural study of the title compound was undertaken as part of an investigation into systems containing multiple hydrogen bonds to oxygen (the ratio of H:O is almost 3:1 in this case). Guanidinium compounds are especially useful in this respect since they invariably form five or six hydrogen bonds per unit charge (Adams & Small, 1976; Adams & Pritchard, 1976).

### Experimental

The sample was prepared by addition of guanidinium carbonate to pyrophosphoric acid, followed by slow evaporation. Small, colourless, needle-shaped crystals

formed which were examined by oscillation and Weissenberg photographs. Symmetry and systematic absences gave the space group as  $P2_12_12_1$  and high- $\theta$  reflexions were used to obtain the cell parameters (Table 1). Equi-inclination intensities were collected for the  $0kl-5kl$  and  $h0l$  levels (for a crystal  $0.6 \times 0.08 \times 0.06$  mm) and these film packs were subsequently scanned on an Optronics P1000 microdensitometer by the SRC Microdensitometer Service at the Atlas Computer Laboratory.

Table 1. *Crystal data*

Space group  $P2_12_12_1$ ;  $a=9.29$  (2),  $b=17.01$  (2),  $c=9.47$  (2) Å (Cu  $K\alpha$ ,  $\lambda=1.5418$  Å),  $Z=4$ ;  $d_o=1.54$ ,  $d_c=1.57$  g cm $^{-3}$