1027. *The Stability of Heteroaromatic Ring Systems.*

By David A. Brown and C. G. McCormack.
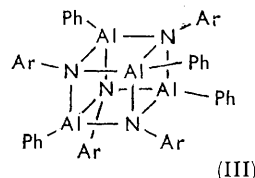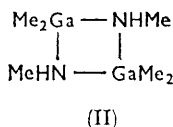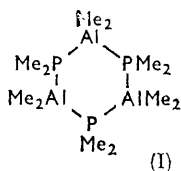
The stability of heteroaromatic ring systems of the type $(RXYR')_3$ (analogous to the borazines), where X and Y are members of Groups III and V, respectively, is discussed in terms of molecular-orbital theory. The suggestion that p_π–p_π overlap is only important for the first members of these groups is shown to be incorrect. From considerations of resonance integrals, valence-state Coulomb terms, and inner shell–outer shell repulsions, it is suggested that the Al–N system is especially unfavourable for conjugation but that B–P analogues of the borazines may be stable.

The past decade has witnessed a large increase in the number of ring systems containing hereroatoms but still retaining aromatic character; these systems are conveniently referred to as heteroaromatic. In particular, borazine, $B_3N_3H_6$, which was once called " inorganic benzene " is now known to be just one example of the extensive isoelectronic sequence (C–C to B–N) which includes B–N analogues of the alkanes, alkenes, and numerous arenes.[1] However, other analogues involving a Group III element (X) and a Group V element (Y) might also be expected in view of the above sequence. It is the purpose of this Paper to discuss the stabilities of heteroaromatic systems of the type $(RXYR')_3$, where R and R' are substituents on atoms X and Y, respectively, and to compare the theoretical conclusions with the available experimental evidence.

Direct addition compounds of the type $R_3XYR'_3$, where R and R' are generally CH_3,

[1] Symposium on Boron-Nitrogen Chemistry, " Advances in Chemistry Series," No. 20, Amer. Chem. Soc., Washington, 1963.

exist for the range X = B, Al, Ga, In, and Tl, and Y = N, P, As, and Sb, and such compounds have formed the subject of a review.[2] Decomposition of these addition compounds to give ring systems occurs for the cases X = B,Y = N, X = Al,Y = N, X = B,Y = P, but only in the B–N case is the compound $(RXYR')_3$ obtained. For X = B,Y = P and X = Al,Y = P, the cyclohexane analogue (I) is obtained,[3] whilst for X = Ga,Y = N a cyclobutane analogue (II) is reported.[4] It was recently shown [5] that decomposition of the addition compounds, X_3Al,NR_3, formed between AlX_3 (X = H, alkyl, aryl, halogen) and amines, results in the formation of polymers of the type $(X_2AlNR_2)_m$ and $(AlNR)_n$. In the latter case, the tetramer has been shown to possess the cubic structure (III).[6]

$$\begin{array}{ccc}
\text{Me}_2 \\
\text{Al} \\
\text{Me}_2\text{P} \quad \text{PMe}_2 \\
\text{Me}_2\text{Al} \quad \text{AlMe}_2 \\
\text{P} \\
\text{Me}_2 \\
\text{(I)}
\end{array}
\qquad
\begin{array}{c}
\text{Me}_2\text{Ga} - \text{NHMe} \\
\mid \qquad \mid \\
\text{MeHN} - \text{GaMe}_2 \\
\text{(II)}
\end{array}
\qquad
\begin{array}{c}
\text{Ph} \\
\text{Al} - \text{N} \quad \text{Ar} \\
\text{Ar} - \text{N} \quad \text{Al} \quad \text{Ph} \\
\text{N} \quad \text{Al} - \text{Ph} \\
\text{Al} - \text{N} \\
\text{Ph} \quad \text{Ar} \quad \text{Ar} \\
\text{(III)}
\end{array}$$

There is thus no evidence to date for the existence of structures of the type $(RXYR')_3$ similar to the borazines and exhibiting some degree of aromaticity. It has generally been assumed in order to explain these facts that $p_\pi–p_\pi$ type overlap is of reasonable magnitude for the first-row elements only;[7] Laubengayer states, for example, that in the aminoalanes, iminoalanes, and aluminium nitride, *i.e.*, in compounds of the type $(R_2AlNR'_2)_n$, $(RAlNR)_n$, and AlN, the aluminium and nitrogen atoms always maintain sp^3 bonding, and that there is no evidence for π-bonding between these atoms. In this Paper, we shall note that it is not correct simply to assume that $p_\pi–p_\pi$ overlap is of importance for the first-row elements only, but, rather, that the instability of the above type of conjugated ring system lies in a number of factors which include valence-state Coulomb terms, inner shell–outer shell repulsions, and σ-bond strengths.

We consider first the simple molecular-orbital theory of the cyclic compounds $(RXYR')_3$; we summarise previous results [8] in Table 1. If the Coulomb term of the $X(np_\pi)$ orbital is denoted as $H_{XX} = H_{CC} + \delta_1\beta_{CC}$, and that of the $Y(n'p_\pi)$ orbital as $H_{YY} = H_{CC} + \delta_2\beta_{CC}$, where β_{CC} is the normal Hückel resonance integral between two adjacent carbon $2p$ -orbitals, then in Craig's notation $\rho_1 = \delta_1 - \delta_2$, the delocalization energy depending on ρ_1 only. The resonance integral $\beta_{XY}(pp)$, between the above orbitals is assumed equal to the standard carbon–carbon integral, β_{CC}. For a planar molecule belonging to the D_{3h} symmetry group, the ground state will be $(1a_2'')^2(1e'')$.[4] The total π-electron energy of the system is simply evaluated by standard procedures in terms of a range of ρ_1 values from which the delocalization energy per π-electron is readily obtained. The values in column 4 of Table 1 are identical with those given graphically in Craig's Fig. 3.[8] It is evident that, even for considerable differences in electronegativity of the two orbitals (X and Y), the resonance energy is appreciable provided that the resonance integral $\beta_{XY}(pp)$ is of reasonable magnitude with respect to β_{CC}; this point is considered further below. The range of δ values appropriate to the first few members of Groups III and V is obtained from the various valence-state Coulomb terms given by Hinze and Jaffé.[9] Comparison of the Coulomb term of the appropriate np_π-orbital with that of the $2p_\pi$-orbital of carbon, with the assumption of a value of 2·5 ev for β_{CC}, permits the calculation of the required δ value. The various

[2] Stone, *Chem. Rev.*, 1958, **58**, 101.
[3] Burg and Wagner, *J. Amer. Chem. Soc.*, 1953, **75**, 3872.
[4] Coates, *J.*, 1951, 2003.
[5] Jones and McDonald, *Proc. Chem. Soc.*, 1962, 366.
[6] McDonald and McDonald, *Proc. Chem. Soc.*, 1963, 382.
[7] Burg, *Chem. Soc. Special Publ.*, No. 15, 1961, p. 17; Laubengayer, *ibid.*, p. 88.
[8] Craig, *J.*, 1959, 997.
[9] Hinze and Jaffé, *J. Amer. Chem. Soc.*, 1962, **84**, 540.

TABLE 1.

Delocalization energies (D.E.) for $(RXYR')_3$.

δ_1	δ_2	ρ_1	D.E. per π-electron (β_{CC})	Inclusion of d_{XZ} orbitals		D.E. per π-electron (β_{CC})
				δ_3	ρ_2	
+1·00	+1·00	0·00	0·333	+1·00	0·00	0·586
,,	,,	,,	,,	0·00	1·00	0·555
,,	,,	,,	,,	−1·00	2·00	0·506
,,	,,	,,	,,	−2·00	3·00	0·471
+1·00	0·00	1·00	0·315	0·00	1·00	0·562
,,	,,	,,	,,	−1·00	2·00	0·528
,,	,,	,,	,,	−2·00	3·00	0·491
,,	,,	,,	,,	−3·00	4·00	0·464
+1·00	−1·00	2·00	0·274	−1·00	2·00	0·504
,,	,,	,,	,,	−2·00	3·00	0·470
,,	,,	,,	,,	−3·00	4·00	0·441
+1·00	−2·00	3·00	0·232	−2·00	3·00	0·457
,,	,,	,,	,,	−3·00	4·00	0·408
,,	,,	,,	,,	−4·00	5·00	0·383
−1·00	+1·00	−2·00	0·274	+1·00	−2·00	0·504
,,	,,	,,	,,	0·00	−1·00	0·436
,,	,,	,,	,,	−1·00	0·00	0·368
,,	,,	,,	,,	−2·00	+1·00	0·335

parameters are listed in Table 2, and it follows that the range of ρ_1 values quoted in Table 1 covers the various elements of interest in Groups III and V.

For elements other than those of the first row, it is necessary to consider the inclusion of *d*-orbitals which it has been suggested [10] may be important for the lower members of these groups. We consider that atom Y possesses available *d*-orbitals and we shall consider only the d_{XZ}-orbital on each Y atom (see Figure). The relative importance of the radial d_{YZ}-orbital in the related phosphonitrilic halides has been the subject of controversy; [11] in our opinion, its inclusion is not important in view of its high energy due to ligand repulsions. We now introduce a third Coulomb term for the $Y(d_\pi)$-orbital: $H_{YY}(d) = H_{CC} + \delta_3\beta_{CC}$, and define $\rho_2 = \delta_1 - \delta_3$, and $\beta_{XY}(pd) = \pm\beta_{CC}$, the sign of $\beta_{XY}(pd)$ depending upon orientation as shown in the Figure. Under D_{3h} symmetry the extra three d_π-orbitals will only interact with the $e''(\pi)$-orbitals of the above p_π–p_π case so that the lowest bonding orbital $(1a_2'')$ is unperturbed. The ground-state configuration is again
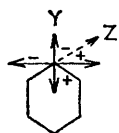
TABLE 2.

Valence-state Coulomb terms.

Element	Valence state	Coulomb term, H_{ii} (ev)	($\beta_{CC} = 2·5$ ev)
C	$tr^1tr^1tr^1p_\pi^1$	11·16	0·00
B	$tr^1tr^1p_\pi^1$	8·33	−1·13
Al	$tr^1tr^1p_\pi^1$	6·43	−1·89
	$tr^1tr^1d_\pi^1$	2·41	−3·50
N	$tr^2tr^1tr^1p_\pi^1$	14·12	+1·18
P	$tr^2tr^1tr^1p_\pi^1$	11·64	+0·19
	$tr^2tr^1tr^1d_\pi^1$	2·91	−3·30

$(1a_2'')^2(1e'')^4$ and the total π-electron energy can be evaluated for a range of values of ρ_1 and ρ_2. The delocalization energies (Table 1, column 7) are then obtained by subtracting the energy of the separate X−Y systems, allowing in this case for the presence of the d_π-orbital. For a given ρ_1 value, it follows that inclusion of the d_{XZ}-orbitals leads to a definite increase in delocalization energy; this result is equally applicable if the *d*-orbital is situated on the more electropositive atom ($\rho_1 \geqslant 0$) or on the more electronegative atom

[10] Craig, Macoll, Nyholm, Orgel, and Sutton, *J.*, 1954, 332.
[11] Dewar, Lucken, and Whitehead, *J.*, 1960, 2423; Craig and Paddock, *J.*, 1962, 4118.

$(\rho_1 < 0)$. As in the comparable $p_\pi\text{–}p_\pi$ case, this conclusion is of course based on the assumption of a reasonably large $\beta_{XY}(pd)$ with respect to β_{CC}.

The simple Hückel molecular-orbital theory thus suggests that heteroaromatic ring systems of the type $(RXYR')_3$ should be stable even when X and Y are of quite different electronegativity; the inclusion of d_π-orbitals on one of the atoms leads to an increase in stability.

TABLE 3.

Overlap integrals and resonance integrals.

Elements (X–Y)	Bond distance (Å)	$S(p_\pi p_\pi)$	$\beta_{XY}(pp)$	$S(p_\pi d_\pi)$	$\beta_{XY}(pd)$
C–C	1·39	0·250	1	—	—
B–N	1·44	0·222	0·893	—	—
Al–N	1·75	0·176	0·648	0·081	0·208
B–P	1·80	0·254	0·909	0·173	0·302
Al–P	2·11	0·268	0·868	—	—
Ga–N	1·76	0·223	—	—	—
B–As	1·90	0·252	—	—	—

Overlap Values.—For the compounds $(RXYR')_3$, only the borazines with X = B, Y = N exhibit some aromaticity, and in these the observed B–N distance [12] is about 10% smaller than the sum of the covalent radii. This bond shortening is close to that observed in benzene. In order to evaluate the overlap integrals, $S(np_\pi n'p_\pi)$ and $S(np_\pi n'd_\pi)$, the above reduction in distance was assumed for all the compounds of interest; the distances thereby obtained are given in column 2 of Table 3. The integrals were calculated according to standard formulæ,[13] and in the case of the $S(2p_\pi 4p_\pi)$ integral the Tables derived by Brown [14] were employed. It is evident from Table 3 that contrary to previous views [7] the $p_\pi\text{–}p_\pi$ overlap integral is of comparable magnitude to that in benzene for all the cases considered in Table 3. It is not legitimate, therefore, to argue against the existence of the above types of heteroaromatic ring on such simple arguments as negligible overlap of the p_π-orbitals. It is, of course, the resonance integral, H_{XY}, which is of real importance since the above conclusions regarding conjugation are based on a molecular-orbital theory in which both $\beta_{XY}(pp)$ and $\beta_{XY}(pd)$ are assumed equal to β_{CC}. A widely accepted approximation to the resonance integral β_{XY} between any two atomic orbitals ϕ_X and ϕ_Y, is that of Wolfsberg and Helmholtz: [15]

$$H_{XY} = k(H_{XX} + H_{YY})S_{XY}$$

where H_{XX} and H_{YY} are the Coulomb terms of ϕ_X and ϕ_Y, respectively, and k is a constant for a given type of interaction. The values of H_{XX} and H_{YY} required are those of the p_π-orbitals in the correct valence state; these are available from previous work [9] and are listed in column 3 of Table 2. Taking the value of β_{CC} as standard, it is evident that $\beta_{AlN}(pp)$ is considerably smaller than β_{CC}, so that in this case the delocalization energy is only about 60% of that shown in Table 1. This conclusion also follows from direct comparison of the $p_\pi\text{–}p_\pi$ overlap values in column 3 of Table 3, which in some cases may be considered to be more reliable than the resonance integral. In general, for a given atom Y, a gradual decrease of β_{XY} is to be expected due to the decrease in H_{XX} as one descends the group; nevertheless, the value of β_{BP} is such as to suggest some stability in this case. Although accurate values for the valence-state Coulomb terms of the lower members of Groups III and V are not available, it follows from the sequence in Table 2 that they will decrease as the electronegativity of the element decreases.

Similar arguments apply to the $p\text{–}d$ interaction. Owing to the diffuse nature of the d_π-orbital, the value of $S(p_\pi d_\pi)$ will be small, and the values in column 5 of Table 3 confirm

[12] Bauer, *J. Amer. Chem. Soc.*, 1938, **60**, 524.
[13] Mulliken, Rieke, Orloff, and Orloff, *J. Chem. Phys.*, 1949, **17**, 1248.
[14] Brown, *J. Chem. Phys.*, 1958, **29**, 1086.
[15] Wolfsberg and Helmholtz, *J. Chem. Phys.*, 1952, **20**, 837.

this. The relevant Coulomb terms of the aluminium and phosphorus d-orbitals can be estimated from the observed spectroscopic p–d separations [16] and the given valence-state Coulomb terms of the corresponding p_π-orbitals; the final values are given in column 3 of Table 2. The resultant resonance integrals are only about 20% of the normal Hückel β_{CC}, and, allowing for the appropriate δ_3 values for these orbitals, it follows that for both aluminium and phosphorus the inclusion of d-orbitals results in an increase in delocalization energy of less than 10% over the corresponding p_π–p_π case. It may be argued that the presence of electronegative ligands would cause a contraction of the d-orbitals [17] with a resultant increase in overlap; however, as discussed by Hudson,[18] this increases the p–d separation and so decreases the Coulomb term, and consequently the resonance integral remains small.

TABLE 4.

Valence-state energies (ev).

Valence state	B	Al	N	P
$tr^1tr^1p_\pi{}^1$	7·398	6·542	—	—
$te^1te^1te^1$	6·586	5·897	—	—
$tr^2tr^1tr^1p_\pi{}^1$	—	—	9·255	5·342
$te^2te^1te^1te^1$	—	—	9·920	5·795

Valence States.—In any discussion of the relative stability of these compounds it is necessary to consider the valence-state energies of atoms X and Y. We assume that X lies in the valence state $tr^1tr^1\pi^1$ and Y in the state $tr^1tr^1tr^2\pi^1$, where tr denotes a trigonal hybrid and π an np_π-orbital of the respective atom. The σ-bond framework of the molecule $(RXYR')_3$ is then composed of dative covalent bonds formed by the overlap of the lone-pair in a trigonal hybrid of Y with the empty trigonal hybrid of X; the π-electron structure arises from the overlap of the singly occupied p_π-orbitals on atoms X and Y. The valence-state energies quoted by Hinze and Jaffé [9] are given in Table 4; the values for boron and aluminium, *viz.*, 7·398 and 6·542 ev, are sufficiently close to suggest that any difference in stability of B–N and Al–N compounds does not arise from these valence-state energies; unfortunately no data are available for the lower members of Groups III and V.

Inner Shell–Outer Shell Repulsions.—It has been suggested [19] that p_π–p_π overlap in the second-row and lower elements is counteracted by inner shell–inner shell repulsions. However, these effects were subsequently shown to be negligible [20] although they are still quoted occasionally [2] as a reason for unstable bonding between the lower elements. We have evaluated the inner shell–inner shell overlap integrals for the members of Groups III and V quoted in Table 3; in all cases the integrals are less than 0·001 and so may be neglected. However, the inner shell–outer shell repulsions are not negligible (Table 5). The calculation of these integrals is again standard following the master formulæ of Mulliken and his co-workers,[13] and all integrals less than 0·01 have been neglected. It is evident that when X and/or Y are second-row elements the inner shell–outer shell overlap integrals are of reasonable size and, moreover, the number of repulsions increases as we descend the groups. These calculations show clearly that the above type of repulsion is an important factor leading to instability in planar conjugated systems of the type $(RXYR')_3$ and that it is of increasing importance for heavier elements.

σ-Bond Strengths.—For a consideration of the σ-bond strengths in these and related compounds, a comparison is made of the group overlap integrals formed between a trigonal hybrid of X and a trigonal hybrid of Y, assuming the same bond distances as in Table 3 for the planar molecule. The results (Table 6, column 2) show that for all the atom pairs

[16] Moore, " Atomic Energy Levels," Nat. Bur. Stand. Circular No. 467, 1949, Vol. I, pp. 164 and 124.
[17] Craig and Magnusson, *J.*, 1956, 4895.
[18] Hudson, *Adv. Inorganic Chem. Radiochem.*, 1963, **5**, 347.
[19] Pitzer, *J. Amer. Chem. Soc.*, 1948, **70**, 2140.
[20] Mulliken, *J. Amer. Chem. Soc.*, 1950, **72**, 4493.

TABLE 5.

Inner shell–outer shell overlap integrals.

Elements	Orbital pair	Overlap integral	Elements	Orbital pair	Overlap integral
B–N	$1s$–$2s$	0·035	Al–N	$2s$–$2s$	0·031
,,	$2s$–$1s$	0·041	,,	$2s$–$2p_\sigma$	0·052
,,	$1s$–$2p_\sigma$	0·059	,,	$2p_\sigma$–$2s$	0·024
,,	$2p_\sigma$–$1s$	0·070	,,	$2p_\sigma$–$2p_\sigma$	0·040
Al–P	$2s$–$3s$	0·037	,,	$3s$–$1s$	0·040
,,	$2s$–$3p_\sigma$	0·063	,,	$3p_\sigma$–$1s$	0·068
,,	$2p_\sigma$–$3s$	0·022	B–P	$1s$–$3s$	0·044
,,	$2p_\sigma$–$3p_\sigma$	0·036	,,	$1s$–$3p_\sigma$	0·075
,,	$3s$–$2s$	0·060	,,	$2s$–$2s$	0·054
,,	$3p_\sigma$–$2s$	0·102	,,	$2s$–$2p_\sigma$	0·084
,,	$3s$–$2p_\sigma$	0·016	,,	$2p_\sigma$–$2s$	0·029
,,	$3p_\sigma$–$2p_\sigma$	0·027	,,	$2p_\sigma$–$2p_\sigma$	0·037
,,	$3p_\pi$–$2p_\pi$	0·011	,,	$2p_\pi$–$2p_\pi$	0·012

TABLE 6.

Hybrid-overlap integrals.

Elements (X–Y)	S(tr–tr)	S(te–te)	Elements (X–Y)	S(tr–tr)	S(te–te)
B–N	0·686	0·594	B–P	0·778	0·678
Al–N	0·567	0·500	Al–P	0·797	0·690

listed the overlap integrals are large, indicating strong σ-bonds in the suggested planar ring system.

Conclusion.—It is evident that there is no single and dominant reason why, to date, analogues of the borazines of the type $(RXYR')_3$, where X and Y are members of Groups III and V, respectively, have not been isolated. In the cases considered above the σ-bond frameworks have been shown to be of comparable stability and the different valence-state energies give no indication of a great difference in stabilities. The first factor which is of importance is the resonance integral $\beta_{XY}(pp)$ which appears especially low for the Al–N compounds and in all cases is lower than the corresponding C–C interaction; moreover, the resonance integral decreases with increasing size of X and Y. It is also necessary to consider the ρ_1 value (Table 1) for any given atom pair since the larger ρ_1 is, the smaller is the delocalization energy; ρ_1 is largest in the case of the Al–N pair, so that for these compounds the low β_{AlN} value and large ρ_{AlN} value suggest strongly that conjugation will be very ineffective. Finally, the presence of inner shell–outer shell repulsions seriously reduces the stability of the above type of compound when X and Y are no longer first members of their respective groups. Since the number of these repulsions increases with increasing size of X and Y, it appears unlikely that stable conjugated compounds of the heavier elements are ever likely to be isolated. One tentative suggestion may be made however; in view of the low ρ_{BP} value and fairly large β_{BP} value, it is possible that boron–phosphorus analogues may occur.

It is interesting to note that of the nitrides of Group III only boron takes up a graphite structure whilst the remainder exhibit a wurtzite structure with tetrahedral co-ordination. This result is in accord with the above discussion. It will be noted from Tables 4 and 6 that for all these systems the tetrahedral overlaps are also large and the valence-state energies lie close to those for the planar trigonal case. In view, then, of the low β_{AlN} value given in Table 3, it is not surprising that the lower nitrides prefer to sacrifice the low delocalization energies of the planar structure for the formation of a fourth and strong covalent σ-bond in a tetrahedral configuration.

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