

Transmission of Substituent Effects through -N-E-N- Systems in Unsymmetrically *N,N'*-Substituted Heteroimidazolines Where E = C, Si, P(III), P(V), and B

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Abstract: The transmission of substituent effects as determined by NMR chemical shifts is used to test the hypothesis of π bonding in the systems -N-E-N- where E = C, Si, P(III), P(V), and B. Unsymmetrically substituted *N,N'*-diphenylimidazolines of the heteroelements phosphorus and boron were chosen in a continuation of previous studies on silicon [C. H. Yoder and J. J. Zuckerman, *Inorg. Chem.*, **6**, 103 (1967)]. Such molecules satisfy the requirement that the substituents be held relatively far from one another on the scale of molecular dimensions, thus minimizing inductive and direct electrostatic field effects as well as magnetic anisotropies which might alter the chemical shifts of the protons under examination. Studies were carried out in mixtures of the compound with the analogous *N-p*-nitrophenyl *N'-p*-dimethylaminophenylimidazolidine as a reference in each case [see structure in Table I; E = P(III), P(V), B; X = *p*-CH₃, *p*-OCH₃, *p*-Cl, *p*-NO₂, and *p*-N(CH₃)₂] and chemical shifts extrapolated to infinite dilution to eliminate bulk magnetic susceptibility effects. In one series of phosphorus(III) imidazolines absolute shifts were measured from TMS and extrapolated to infinite dilution as a check. Chemical shift differences in the dimethylamino group protons were measured to better than ± 0.10 Hz. Transmission across analogous unsymmetrically substituted, acyclic *N,N'*-diphenylethylenediamines is negligible. Shifts for each series of heteroimidazolines are shown to correlate with the Hammett σ constant for each substituent but to correlate less well with either σ_I or σ_R . Shifts for all the series fall on the same straight line for E = CH₂, Si(CH₃)₂, PC₆H₅, P(O)C₆H₅, and BC₆H₅ with $\rho = -1.22$ Hz. This finding is discussed in terms of possible (*p*→*p*)- π bonding for E = boron, (*p*→*d*)- π bonding for silicon and phosphorus, hyperconjugation for carbon, orbital coupling through the CH₂CH₂ bridge, or a direct, through-space -N--N- interaction, the last of which is preferred. The syntheses of six phosphorus(III), four phosphorus(V) oxide, and three novel unsymmetrically substituted boron imidazolines are described.

In 1967 Yoder and Zuckerman¹ published the results of experiments designed to test for the presence of a continuous (*p*→*d*)- π bond in the ---N---Si---N--- system. Their magnetic resonance studies were based upon the premise that a distinguishing feature of a delocalized π system is the ability to transmit substituent electrical effects to a greater extent than a saturated system of similar length. Comparisons of this sort are found between the substituent-induced changes in benzoic acid dissociation constants vs. the much smaller effect seen in comparable saturated systems which hold the active centers in a rigid way at an equivalent distance: *trans*-4-substituted-cyclohexanecarboxylic acids,² 4-substituted-bicyclo-[2.2.2]octane-1-carboxylic acids,³ 4-substituted-bicyclo-[2.2.1]heptane-1-carboxylic acids,⁴ *trans*-2-substituted-phenylcyclopropanecarboxylic acids,⁵ 1,3-disubstituted-adamantanes,⁶ and various cyclopropanes and heterocyclic three-membered rings.⁷ The use of NMR spectroscopy allows the determination of substituent effects in ground state, neutral molecules, thus avoiding the complications inherent in chemical reactions or rate studies, although NMR results do parallel those from chemical studies on similar systems. Our experiments involve measuring the substituent-induced shift transmitted through the ---N---E---N--- system with respect to the saturated ---N---C---N--- case. The chief requirement for the test molecule of choice was that the substituents be held as far apart from one another on the scale of molecular dimensions as possible, while still allowing the smallest shifts to be measured outside experimental error. In this way both the inductive and direct field effects would be minimized as well as any through-space effect which might alter the magnetic environment of the protons of interest.

The imidazolidine ring system shown above nicely meets these requirements. The *N*-phenyl para substituents attached at the 1,3-positions on the ring are held relatively far apart, and

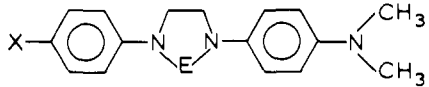
magnetic anisotropy effects should be constant through the series of compounds studied. The para substituent, X, was varied in each series, and the effect of changing X on the proton chemical shift of the dimethylamino group attached on the other side of the molecule was taken as a measure of the transmission of substituent effects across the ring. The transmission as measured by this method in unsymmetrically substituted acyclic *N,N'*-diphenylethylenediamines is negligible for *N-p*-nitrophenyl-*N'-p*-methoxyphenyl- as against *N,N'*-bis(*p*-methoxyphenyl)ethylenediamine, the pair of compounds expected to exhibit the greatest shift effect.¹

In the earlier study no enhancement in the change of $\delta[\text{N}(\text{CH}_3)_2]$ was seen in the silicon compounds over their saturated carbon analogues. In the present work we have extended the measurements to P(III), P(V), and B by the synthesis of six phosphorus(III), four phosphorus(V) oxide, and three novel unsymmetrically *N,N'*-diphenyl-substituted boron imidazolines, as an extension of our previous reports on silicon,^{8,9} germanium,⁸ boron,¹⁰⁻¹² and phosphorus¹⁰⁻¹² analogues, and we offer a new interpretation which can be applied to all the available data.

Results

In one series of imidazolines, where E = P(C₆H₅), we have measured the absolute chemical shifts of the N(CH₃)₂ protons at 60 MHz vs. a TMS standard and extrapolated the results to infinite dilution. These data are listed in Table I along with the shifts of the E = P(O)C₆H₅ and B(C₆H₅) and the Hammett σ values we used. The chemical shift data for the P(III) series give a satisfactory straight line when plotted as $\Delta\delta \approx \rho\sigma + C$ ($\rho = -1.28$; correlation coefficient, *r*, is 0.990). The differences in chemical shift value, $\Delta\delta$, for the P(V) and B(C₆H₅) imidazolines are the result of measurements on mixtures of these unsymmetrically substituted analogues containing the substituent X, as against the corresponding *N-p*-nitrophenyl-*N'-p*-dimethylaminophenylimidazolidine as reference in

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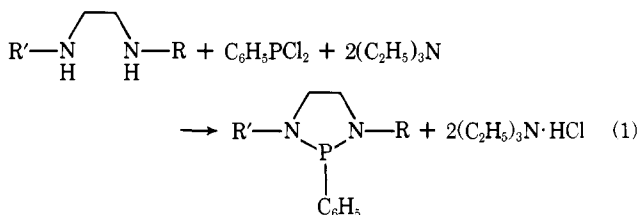
Table I. $N(CH_3)_2$ Proton Chemical Shift Changes with Substituent in Hz at 60 MHz^a


X	σ^b	δ	$\Delta\delta, E =$		
			P(C ₆ H ₅)	P(O)-C ₆ H ₅	B(C ₆ H ₅)
<i>p</i> -NO ₂	+0.778	-173.4 ^c	0	0	0
<i>p</i> -Cl	+0.227	-172.8	0.6	0.9	0.95
<i>p</i> -CH ₃	-0.170	-172.3	1.1		
<i>p</i> -OCH ₃	-0.268	-172.0	1.4	1.4	1.25

^a ±0.07 Hz at infinite dilution. ^b Hammett σ constants from H. H. Jaffe, *Chem. Rev.*, 53, 191 (1953). ^c With reference to TMS at infinite dilution.

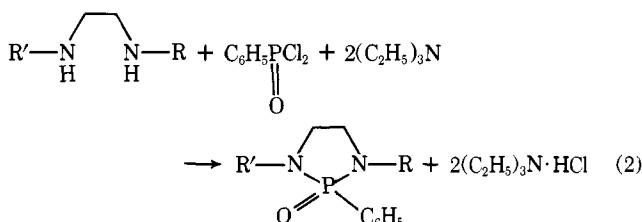
deuteriochloroform. The data in Table I along with the results previously reported in ref 1 are plotted in Figure 1 against the Hammett σ values, and all five series of data are found to fall upon the same straight line with a reaction constant, ρ , for the system of -1.22 Hz.¹³ The constants σ_R and σ_I give a less satisfactory fit. The regression analysis data, n , number of compounds, C , intercept, ρ , parameter of the equation $\Delta\delta = \rho\sigma$, r , correlation coefficient, and S , standard deviation of the residuals are: for E = CH₂, 3, 0.988, -1.208, 0.992, 0.111; for Si(CH₃)₂, 3, 0.956, -1.109, 0.960, 0.170; for BC₆H₅, 3, 1.029, -1.21, 0.966, 0.168; for PC₆H₅, 4, 0.956, -1.278, 0.990, 0.085; for P(O)C₆H₅, 3, 1.10, -1.34, 0.991, 0.094; and for all the data taken together, 16, 0.999, -1.216, 0.981, 0.109.

Syntheses and Characterization. Phosphorus Imidazolidines. As with the symmetrically substituted compounds,¹⁰ the unsymmetrical 1,3-diaza-2-phospholidines¹⁴ and -phospholidine 2-oxides¹⁴ were prepared by amination of the corresponding phosphorus dichloride by the unsymmetrically *N,N'*-disubstituted-ethylenediamine.¹⁵ We have prepared six unsymmetrically substituted phosphorus(III) imidazolidines and four phosphorus(V) imidazolidines by this route as shown in eq 1 and 2. The Lewis base triethylamine was added in each case



- I: R = *p*-NO₂C₆H₄; R' = *p*-(CH₃)₂NC₆H₄
 II: R = *p*-CH₃OC₆H₄; R' = *p*-(CH₃)₂NC₆H₄
 III: R = *p*-ClC₆H₄; R' = *p*-(CH₃)₂NC₆H₄
 IV: R = *p*-CH₃C₆H₄; R' = *p*-(CH₃)₂NC₆H₄
 V: R = *p*-CH₃C₆H₄; R' = *p*-NO₂C₆H₄
 VI: R = *p*-CH₃OC₆H₄; R' = *p*-NO₂C₆H₄

and



- VII: R = *p*-ClC₆H₄; R' = *p*-(CH₃)₂NC₆H₄
 VIII: R = *p*-CH₃OC₆H₄; R' = *p*-(CH₃)₂NC₆H₄
 IX: R = *p*-NO₂C₆H₄; R' = *p*-(CH₃)₂NC₆H₄
 X: R = *p*-NO₂C₆H₄; R' = *p*-CH₃OC₆H₄

to facilitate the reaction by taking up the hydrogen chloride liberated. The reactions are slightly exothermic, but refluxing

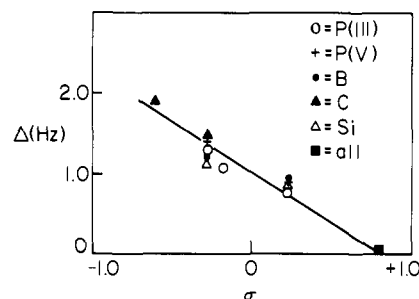
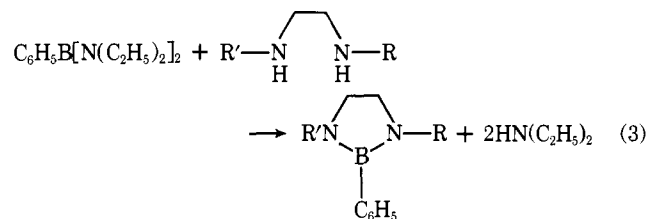


Figure 1. Correlation of $N(CH_3)_2$ proton NMR chemical shifts with the Hammett σ constants of X.

for 4–6 h is necessary to drive them to completion. Initial yields were essentially quantitative, as determined from the yield of triethylamine hydrochloride produced; but the final recoveries after recrystallization varied in the range 30–60%. Both the phosphorus(III) and phosphorus(V) imidazolidines are air stable.

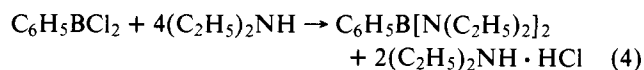
The physical properties and microanalytical data for these compounds are listed in Table II.

Boron Imidazolidines.¹⁴ Three new unsymmetrical boron imidazolidines have been prepared by the transamination of bis(diethylamino)phenylborane with unsymmetrically *N,N'*-diphenyl-substituted ethylenediamines:¹⁵



- XI: R = *p*-NO₂C₆H₄; R' = *p*-(CH₃)₂NC₆H₄
 XII: R = *p*-CH₃OC₆H₄; R' = *p*-(CH₃)₂NC₆H₄
 XIII: R = *p*-ClC₆H₄; R' = *p*-(CH₃)₂NC₆H₄

The bis(diethylamino)phenylborane was prepared from (dichloro)phenylborane and diethylamine by the method of Nidenzu et al.¹⁶



The physical properties and microanalytical data for these compounds are listed in Table II.

Proton NMR data are listed in Table III. The extremely complex resonances of the aromatic protons arise from the presence of several differently substituted aromatic rings and are excluded from the listing. The spectra of the methylene bridge protons of the boron imidazolidines are strikingly simple, all being sharp singlets with no coupling to, or quadrupolar broadening by, ¹¹B through the -B-N-CH₂- system observed. The other portions of the spectra were similar to those of the corresponding phosphorus(III) imidazolidines. We have previously pointed out¹⁰ that the methylene bridge protons in symmetrically *N,N'*-disubstituted-phosphorus(III) imidazolidines display either a sharp doublet for R = R' = C₂H₅,¹⁷ C₆H₅, and C₆H₄CH₃ or a multiplet pattern for R = R' = CH₃ and *p*-C₆H₄OCH₃. The phosphorus-31 coupled doublets were interpreted in terms of either complete ring planarity, ring planarity about either the nitrogens or the phosphorus with rapid inversion occurring about the other element, or rapid inversion about both the nitrogen and the phosphorus. The multiplet resonance, on the other hand, would arise if the inversion at phosphorus were slow, or the inversions at the nitrogens were slow and unconcerted, or if the *N*-substituents were in a fixed trans position. The multiplet resonance

Table II. Physical Properties and Analytical Data of the Phosphorus and Boron Imidazolidines

Compd	Yield, %	Mp, °C	Color	Found			Found Calcd Mol wt
				C	H	N	
I	50	191-193	Brown	65.96 65.02	6.22 5.70	14.63 13.79	408 406.4
II	41	193-194	White	70.14 70.57	6.78 6.69	10.63 10.73	390 391.5
III	34	195-196	White	65.82 66.75	6.08 5.86	10.62 10.61	400 395.9
IV	42	186-187	White	72.71 73.58	6.92 6.98	10.80 11.19	360 375.5
V	60	182-184	Brown	64.48 66.84	5.73 5.34		
VI	45	128-130	Brown	61.43 64.12	5.38 5.12		
VII	30	244-246	White	63.29 64.16	5.77 5.63	10.27 10.20	
VIII	45	216-218	Light pink	68.19 67.80	6.40 6.43	8.94 10.31	
IX	50	226-228	Light green	60.02 62.55	5.47 5.49	12.62 13.26	
X	40	215-216	Yellow	61.37 61.61	5.11 4.92		
XI	96	155-158	Brown	68.99 68.41	6.15 6.00	13.50 14.50	374 386.3
XII	95	110-112	White	72.52 74.40	7.17 7.06	10.88 11.32	342 371.3
XIII	90	79-80	White	69.23 70.33	6.64 6.17	12.20 11.18	340 375.7

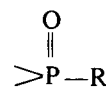
Table III. Proton NMR Chemical Shift Values in $\tau^{a,b}$

Compd	N(CH ₃) ₂	N-CH ₂ -, M ^c	CH ₃	OCH ₃
I	7.12	6.29 br s		
II	7.16	6.41 br s		6.29
III	7.13	6.36 br s		
IV	7.14	6.39 br s	7.75	
V		6.20 br s	7.72	
VI		6.28 br s ^d		6.24 ^d
VII	7.22	6.14 d, $\Delta = 7.5$ Hz		
VIII	7.22	6.14 d, $\Delta = 7.5$ Hz		6.35
IX	7.21	6.11 d, $\Delta = 5$ Hz		
X		6.02 d, $\Delta = 7.5$ Hz		6.29
XI	7.18	6.07		
XII	7.19	6.11		6.30
XIII	7.19	6.11		

^a Phosphorus(III) and -(V) compounds were saturated solutions in CDCl₃, boron compounds were ~20% solutions in CDCl₃, and all τ values were measured with TMS as internal standard; values are concentration dependent. ^b Measured at 60 MHz at ambient temperature. ^c M = multiplicity; br s = broad singlet; d = doublet; Δ = separation between the peaks in the doublet. ^d Signals are partially overlapped.

of the methylene bridge protons is an ABA'B'X situation arising from the destruction of the plane of symmetry containing the ring by the pyramidal phosphorus. Our recent x-ray structure¹⁸ of 1,3-bis(*p*-tolyl)-2-phenyl-4,5-dihydro-1,3-diaza-2-phospholidine reveals an almost planar ring containing trigonal nitrogens but pyramidal phosphorus. Compounds giving rise to a sharp doublet methylene bridge resonance must thus undergo rapid inversion about phosphorus in solution. The multiplet observed for the *p*-NC₆H₄OCH₃ case could also arise from slow rotation of the bent methoxyl groups about the *p*-O or *N*-phenyl bonds. Such a situation would give rise to the mutual coupling of an A₂B₂X pattern.¹⁰ The N,N'-unsymmetrically substituted compounds reported here must neces-

sarily give rise to mutually coupled A₂B₂X patterns as well. Broad resonances are observed for all the phosphorus(III) compounds, while the phosphorus(V) compounds gave broad doublets. Reduction in the symmetry of the rings in these latter compounds occurs by virtue of both the unsymmetrical nature of the N,N' substitution as well as the inherent nonequivalence of the two ring faces because of the



system, thus destroying both perpendicular mirror planes and making each of the four methylene bridge protons inequivalent in an AA'BB'X situation. Comparison of the phosphorus(III) and phosphorus(V) spectra shows that the magnetic differences, arising from freezing the configuration of the phosphorus atom by substituting oxygen for the lone pair of electrons in the phosphorus(V) examples, are larger than those produced by the unsymmetrical N,N' substitution. An alternative explanation of the broad doublet resonances would involve the larger ³J(³¹P-N-C-¹H) coupling constants expected for phosphorus(V).¹⁹

The sharp singlet methylene bridge proton resonances of the boron derivatives can be rationalized on the basis of planar configurations about both the nitrogen and boron atoms to give a planar ring or by rapid oscillation about the tetrahedral nitrogens with attached planar boron with respect to the NMR time scale. However, gas-phase electron diffraction experiments show that 1,3-dimethyl-2-chloro-4,5-dihydro-1,3-diaza-2-borolidine is essentially planar with only a slight deviation from planarity at the nitrogen atoms (the sum of the angles being 325.8°).²⁰

In the infrared spectra of the boron imidazolidines we observed two new bands, one at ca. 1500 and one in the range 1305-1315 cm⁻¹, both of which disappeared on hydrolysis in air. Niedenzu et al.¹⁶ suggest that absorptions in the region 1300-1450 and at ca. 1500 cm⁻¹ are associated with boron-nitrogen stretching. New bands which also disappeared on hydrolysis were found at ca. 750 cm⁻¹.

Infrared $\nu(\text{P}=\text{N})$ stretches in phosphonitrilics lie in the range 1400–1200 cm^{-1} , but the phosphorus–nitrogen bond in our systems is one of the longest found among the single bonds at 1.700 Å.¹⁸ Bellamy²¹ attributes absorptions in the 750–680 cm^{-1} range to $\nu(\text{P}-\text{N})$, and a band at 695 cm^{-1} not present in the diamine appears in all the phosphorus imidazolidines. Bands at 675, 645, and 630 cm^{-1} also appear in the spectra of 1,2,3-trimethyl- and 1,2-dimethyl-2-phenyl-4,5-dihydro-1,3-diaza-2-phospholidine.¹⁰ These bands disappear on hydrolysis in air.

Discussion

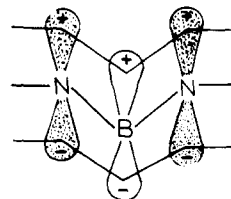
The N,N' -diphenylimidazolidines can be considered as consisting of two aniline moieties connected by *cis*-methylene bridges such that their nitrogen atoms are held in juxtaposition for simultaneous bonding with some third atom, E. As is well-known, para substitution in aniline brings about strong changes in the properties of the nitrogen atom. The most recent and compelling evidence derives from NMR spin–spin coupling studies of aniline-¹⁵N derivatives variously substituted on the phenyl ring, where large changes in $J(^{15}\text{N}-\text{H}^1)$ are induced by para substitution and follow roughly the Hammett σ value of the particular substituent.²² Thus we will assume the existence of a continuous π -electrical system, uninterrupted by nodes, which extends from the para substituents used in our study to the ring nitrogen atoms.

The structure of aniline has been determined in the gas phase by microwave methods. Nitrogen occupies the apex of a somewhat flattened pyramid with $\angle\text{HNH} \approx 114^\circ$.²³ However, although electric dipole moment studies suggest the $\text{E} = \text{CH}_2$ ring to be nonplanar,²⁴ our recent x-ray structure of the $\text{E} = \text{P}(\text{C}_6\text{H}_5)$, 1,3-bis(*p*-tolyl)-2-phenyl-4,5-dihydro-1,3-diaza-2-phospholidine¹⁸ reveals an almost planar ring containing trigonal nitrogen (the sum of the angles being 358.9°). The *N*-phenylene rings are close to coplanarity with the central, imidazolidine ring. The phosphorus(III) atom, by contrast, is pyramidal (the average bond angle being ca. 100°). The trigonal planar hybridization of the nitrogen indicated by this result would be expected to favor *N*-phenylene rings which are coplanar with the nitrogen geometry if nitrogen lone pair density in the unhybridized 2p orbital is delocalized into the antibonding orbitals of the aromatic ring. The boron atom in our boron imidazolidines is undoubtedly at the center of a trigonal plane, and 1,3-dimethyl-2-chloro-4,5-dihydro-1,3-diaza-2-borolidine is planar in the gas phase (e.d.), deviating only slightly from planarity at the nitrogen atoms.²⁰ Excluding the $\text{E} = \text{P}(\text{V})$ case in which the methylene bridge protons necessarily form an AA'BB'X pattern, the NMR evidence is consistent with planar structures for all the symmetrically N,N' -disubstituted derivatives.^{8b}

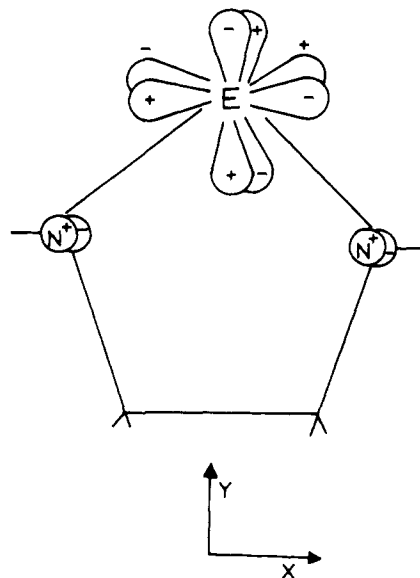
Thus the structures of the boron²⁰ and phosphorus(III)¹⁸ derivatives and other evidence from NMR studies indicate that there is no steric inhibition to resonance interactions in the *N*-phenylene systems and that a continuous π corridor exists to bring the substituent effect information to the central ring. The result of the simultaneous coplanarity of the three rings¹⁸ is then to produce charge separation at the two nitrogen atoms of the imidazolidine ring in the N,N' -unsymmetrically substituted derivatives studied here. The substituent effect information is then transmitted from nitrogen to nitrogen to affect the NMR chemical shift of the dimethylamino protons across the system, but as our results show, the transmission of the substituent effect is the same for the heterocycles containing $\text{E} = -\text{CH}_2-$, $-\text{Si}(\text{CH}_3)_2-$, $-\text{BC}_6\text{H}_5-$, $-\text{PC}_6\text{H}_5-$, or $-\text{P}(\text{O})\text{C}_6\text{H}_5-$ groups.

We will consider first a transmission pathway through the bonds of the ---N---E---N--- system. This portion of our boron imidazolidine is a fragment of a borazine ring system in which

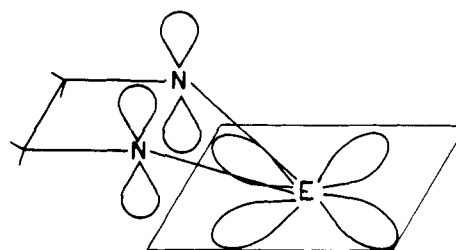
delocalization of the π electrons is indicated from MO calculations²⁵ and experimental results for the transmission of substituent effects through the B_3N_3 ring.²⁶ In our situation the empty 2p orbital on boron could overlap with the filled 2p orbitals on the trigonal planar nitrogen atoms to delocalize charge density from one to the other:



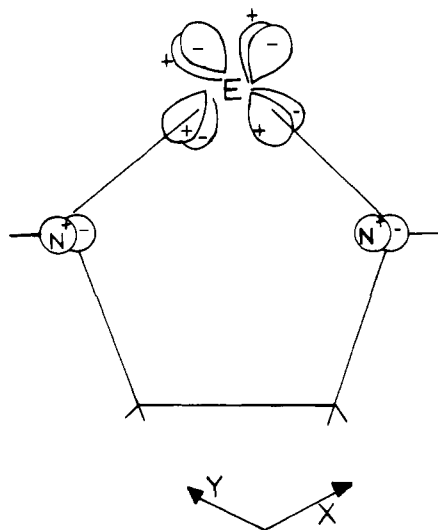
The elements silicon and phosphorus possess empty, low-lying 3d orbitals which could be utilized in at least two ways to form a continuous ---N---E---N--- system. In the first two, the lobes of a single, empty 3d orbital of E overlap both filled 2p orbitals of the nitrogen atoms by virtue of being interposed toward the center of the ring between them:²⁷



In the limit of strong π overlap a pure p orbital on nitrogen would be used, thus stabilizing a planar ring and giving rise to a three-center molecular orbital antisymmetric with respect to reflection in the plane of the ring but shorter in length than one passing by way of the E atom center. In a slightly nonplanar ring two lobes of a single 3d orbital of atom E could overlap the lower or upper lobes of the nitrogen lone pair orbital:



The resulting bond would neither be antisymmetric with respect to reflection in the plane of the ring nor symmetric with respect to the E–N axis, but such interaction with two lobes of the same d orbital would form a three-center molecular orbital not occupying the same region of space as the E–N σ bond. Oscillation about incompletely planar nitrogen atoms would break and re-form a similar molecular orbital on the other side of the ring. Use of a single $3d_{z^2}$ orbital would not result in bonding (by symmetry), nor would the use of two orthogonal 3d orbitals:



since the pathway would be disrupted by the nodal plane between them. In the $E = \text{CH}_2$ case a hyperconjugative mechanism for transmission is possible which resembles the scheme drawn for $E = \text{B}$ above.

Using these three familiar bonding schemes, $(p \rightarrow p) - \pi$ for boron, $(p \rightarrow d) - \pi$ for silicon and phosphorus, and hyperconjugation for carbon to rationalize our results requires that we accept that all three operate to the same extent, however. A more attractive alternative would be a single explanation which could be applied to all the derivatives studied in common. Two such possibilities are available.

Ethylenediamine exists in the gas phase exclusively as the gauche conformer with an N-C-C-N dihedral angle measured from the cis position as 64° .²⁴ Closing the imidazolidine ring has the effect of bringing the two nitrogen atoms closer together in a region where their lone-pair electrons can interact. Theoretical calculations by Hoffmann et al.²⁹ and photoelectron spectroscopic studies by Heilbronner et al.^{30,31} have indicated a direct N...N through-space interaction in bridgehead diazabicycloalkanes. The interaction of the lone pair splits the energies of the two topmost occupied orbitals by 0.5 eV in ethylenediamine but by 1.5 eV in 1,4-diazabicyclo[2.2.2]octane (DABCO).³⁰ In their analysis Hoffmann et al. resolved the interaction into two distinct symmetry-controlled mechanisms, a direct through-space and a through-bond hyperconjugative effect,³² which can work in opposite directions. In DABCO the through-bond interaction was calculated to be dominant, with the through-space term small and in the opposite direction. Replacing the two-carbon bridges (the most favorable case for through-bond interaction) by one-carbon bridges tends to reduce the through-bond interaction and strengthen the through-space interaction since the lone-pair electrons would be brought closer together.²⁹ Piperazine, more like our imidazolidine system than DABCO, shows zero splitting,³⁰ and presumably the two mechanisms are in balance. In our system one of the two-carbon bridges is replaced by a single atom, E, and the two nitrogen atoms are brought closer in space still to allow for a through-space interaction which apparently predominates in all the systems we have studied.

Experimental Section

Proton NMR measurements were recorded on a Varian Associates A60-A spectrometer in deuteriochloroform with tetramethylsilane (TMS) as the internal standard. Infrared measurements were recorded on a Beckman IR-10 spectrometer and were calibrated with polystyrene film. Molecular weights were determined on a Hewlett-Packard vapor pressure osmometer Model 301A using benzene as solvent. Melting points were recorded on a Townson and Mercer type 5 melting point block and are reported uncorrected. Microanalyses were performed by Instral Laboratory Inc., Rensselaer, N.Y. All

operations were carried out under nitrogen. Reagent grade benzene was dried by refluxing over sodium wire and *n*-hexane over potassium, and both were distilled prior to use.

The unsymmetrically *N,N'*-diphenyl-substituted ethylenediamines were prepared according to methods already described.¹⁵

Preparation of 1,2,3-Triaryl-1,3-diaza-2-phospholidines (I-X). The appropriate unsymmetrically *N,N'*-diphenyl-substituted ethylenediamine (0.01 mol) was dissolved in 30–40 ml of benzene in a three-necked flask and triethylamine (2.23 g, 0.022 mol) was added. Dichlorophenylphosphine or dichlorophenylphosphine oxide (0.01 mol) dissolved in 10 ml of benzene was added dropwise with magnetic stirring, and the mixture was then refluxed for 4–6 h. The reaction mixture was filtered while still warm and the precipitate of triethylamine hydrochloride was washed with warm benzene. After concentration of the filtrate under reduced pressure and subsequent refrigeration, the crystals of the diazaphospholidine appeared. These crystalline compounds were recrystallized from benzene after separation and then dried in a vacuum desiccator. Because the starting diamines and the product phosphorus imidazolidines had similar solubilities, the initial products were slightly impure. The yields after recrystallization were in the range of 30–60%. Physical properties, yields, and analytical data of these compounds are recorded in Table II.

Preparation of 1,2,3-Triaryl-1,3-diaza-2-borolidines (XI–XIII). The appropriate unsymmetrically substituted *N,N'*-diarylethylenediamine¹⁵ (0.005 mol) was dissolved in 75 ml of dry benzene, and bis-(diethylamino)phenylborane (1.16 g, 0.005 mol) dissolved in 25 ml of dry benzene was added dropwise with magnetic stirring and then refluxed for 5 h. After cooling, the reaction mixture was filtered to remove any unreacted ethylenediamine. The filtrate was evaporated to dryness under reduced pressure, and the solid residue thus obtained was washed with *n*-hexane and dried in a vacuum desiccator. The physical properties, yields, and microanalytical data are listed in Table II.

Acknowledgment. Our work is supported by the National Science Foundation through Grant GP-16,544. We thank Professor C. H. Yoder of Franklin & Marshall College for helpful discussions.

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Mechanism of the Structural Transformations of Anthocyanins in Acidic Media

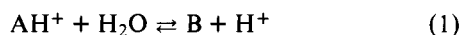
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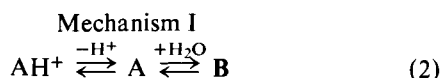
Abstract: In acidic aqueous media (pH 1–6), there are three forms of malvin: the flavylium cation AH^+ , the carbinol B, and the quinonoidal base A. Equilibrium between the two neutral forms occurs exclusively by way of the flavylium cation with a constant $K_{23} = [B]/[A] = 1.6 (\pm 0.5) \times 10^2$ at 4 °C. Contrary to all previous reports the quinonoidal base does not hydrate. The neutralization of this base by the hydronium ion is endothermic; the associated rate constant k_{21} is $1.4 (\pm 0.1) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ at 6.5 °C. The rate constant for deprotonation of the cation by the solvent k_{12} is $1.8 (\pm 0.1) \times 10^4 \text{ s}^{-1}$ at the same temperature. Hydration of the flavylium cation involves the formation of a C–O bond and a proton transfer. The rate constant k_{13} for nucleophilic addition of water to the flavylium cation is $4.7 (\pm 0.2) \times 10^{-2} \text{ s}^{-1}$ at 4 °C; for the reverse reaction the rate constant k_{31} is $2.6 (\pm 0.1) \text{ M}^{-1} \text{ s}^{-1}$ at the same temperature. The existence of very small amounts of a third neutral form, the chalcone C, a prototropic tautomer of the carbinol B, is considered.

Since the work of Willstätter¹ and Robinson,² it has been known that anthocyanins are responsible for a variety of beautiful plant colors. Although they are found in every part of a plant, they are most obvious in flowers and fruits.³ Extending our knowledge of the biological phenomena involved requires a good understanding of the physicochemical properties of these compounds and especially of their reactivity toward chemical agents found in nature.

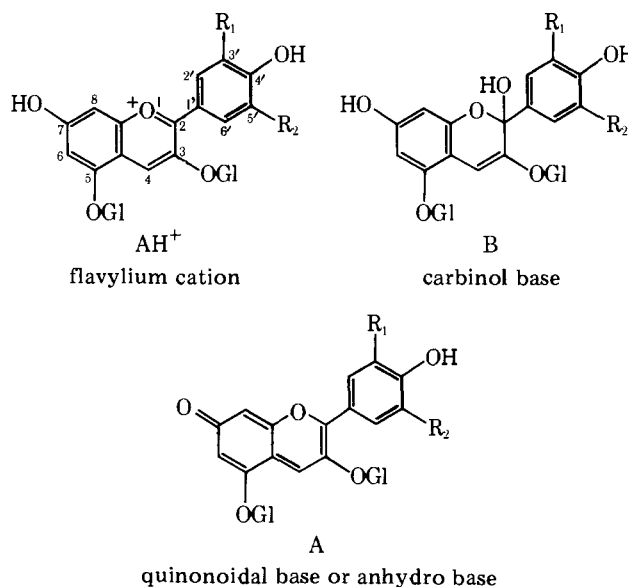
Depending on the degree of acidity or alkalinity, anthocyanins adopt different chemical structures. Each of these structures presents, in the visible region, a characteristic absorption spectrum. At present, it is generally accepted that there is an equilibrium between the flavylium (2-phenylbenzopyrylium) cation AH^+ and the carbinol B in acidic media (eq 1).



Sondheimer⁴ was the first to measure the equilibrium constant of this reaction in the case of pelargonidin 3-monoglucoside ($R_1 = R_2 = H$; OH at position 5). The mechanism generally proposed⁵ supposes the existence of a transient species, the anhydro base A, obtained by deprotonation of the flavylium cation. This quinonoidal base would be converted into the carbinol B by addition of water (mechanism I, eq 2).



This mechanism has been elaborated on the basis of somewhat superficial observations; i.e., when the acidity of the medium is rapidly and sufficiently diminished, the flavylium cation instantaneously turns into the anhydro base which, *apparently*, slowly hydrates into the carbinol.⁶ The following reasons, however, cause us to doubt the validity of this mechanism:



(a) According to mechanism I (eq 2), any shift from left to right is always assumed to make anhydro base show up, no matter what the final medium acidity value (the proton transfer reaction is very fast as compared to the hydration reaction). However, it has been shown⁵ that there is an acidity threshold (pH 3–4), below which anhydro base formation is no longer observed and that, despite this fact, the final product is indeed the carbinol.

(b) The flavylium cation–carbinol equilibrium exists even when the cation lacks a hydroxyl group. Some authors⁷ consider that in this last case direct reaction of the cation with hydroxyl ion takes place.

These indications point to the existence of a pathway dif-