Transmission of Substituent Effects Through –N–E–N– Systems in which E = C, Si, P^{III}, P^{V}, and B

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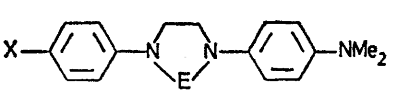
Summary The transmission of substituent effects across various *N*-phenyl-substituted-*N'*-*p*-dimethylamino-phenyl heteroimidazolidines is the same for all the heteroatoms [$-CH_2-$, $-SiMe_2-$, –PPh–, –P(O)Ph–, and –BPh–] studied.

NUCLEAR magnetic resonance chemical shifts are used to determine the transmission of substituent effects in the systems –N–E–N– where E = $-CH_2-$, $-SiMe_2-$, –PPh–, –P(O)Ph–, and –BPh–. Unsymmetrically substituted *NN'*-diphenylheteroimidazolidines with the heteroatoms phosphorus(III), phosphorus(V), and boron were chosen to test the possibility of π-bonding in a continuation of previous studies on silicon.[1] Such molecules satisfy the requirement that the substituent groups 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*-dimethylamino-phenylimidazolidine, the derivative whose substituents have the most disparate Hammett σ-constants,[2] as a reference (X = NO_2) in each case. Chemical shifts were extrapolated infinite dilution to eliminate bulk magnetic susceptibility to effects. Chemical shift differences in the Me_2N protons could be measured to an accuracy of > 0·10 Hz at 60 MHz by this technique. Transmission across analogous unsymmetrically substituted, acyclic *NN'*-diphenylethylenediamines is negligible.



E = P^{III}: X = Me, Cl, MeO, and NO_2
E = P(O)Ph: X = Cl, MeO, and NO_2
E = BPh: X = Cl, MeO, and NO_2

The shifts for each series of heteroimidazolidines gave linear correlations with the Hammett σ-constant[2] for each substituent, but surprisingly the data for all the series fall on the same straight line (see Figure) with a reaction constant, ρ, for the system of −1·27 ± 0·05 Hz.

The *NN'*-diphenylimidazolidines can be considered as consisting of two aniline units connected by *cisoid*-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 marked changes in the chemistry of the nitrogen atom which lies at the apex of a somewhat flattened pyramid in the gas phase structure (microwave).[3] In the heteroimidazolidines, on the other hand, the nitrogen is trigonal planar [E = PPh (*X*-ray),[4] (electron diffraction)[5]], and in the *NN'*-bis(*p*-tolyl)phosphorus(III) imidazolidine the *N*-phenylene rings are coplanar with the central ring.[4] A continuous π-corridor can thus be assumed to extend from the *para*-substituents to the ring nitrogen atoms, producing charge separation at the two nitrogen atoms. The substituent effect information could then be transmitted from nitrogen to nitrogen, but transmission pathways through the –N–E–N– system utilizing $(p \rightarrow p)$-π-bonding for boron, $(p \rightarrow d)$-π-bonding for silicon and phosphorus, and hyperconjugation for carbon would have to operate to the same extent to rationalize our results. The following alternative interpretation could be applied to all the derivatives studied, however.

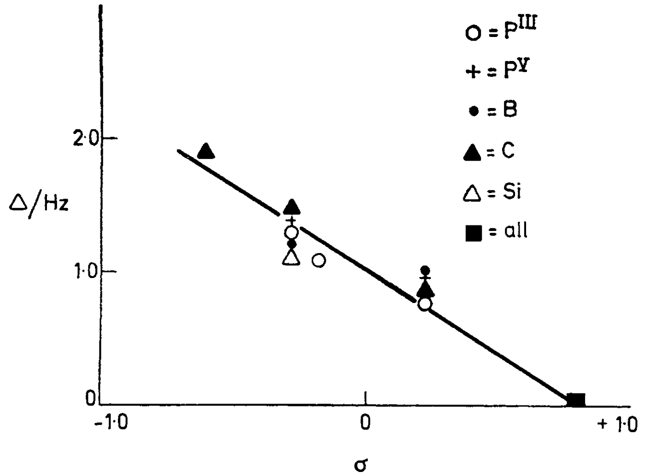


FIGURE. Correlation of $-NMe_2$ ^1H n.m.r. chemical shifts with the Hammett σ-constants of X. The regression analysis data: *n*, number of compounds, *C*, intercept, ρ, parameter of the equation $\delta = \rho\sigma$, *r*, correlation coefficient, *S*, standard deviation of the residuals, are, for E = CH_2: 3, 1·075, −1·38, 0·999, 0·004; $SiMe_2$: 3, 0·956, −1·09, 0·960, 0·170; BPh: 3, 1·029, −1·20, 0·966, 0·168; PPh: 4, 0·969, −1·19, 0·991, 0·076; P(O)Ph: 3, 1·10, −1·34, 0·991, 0·094; and for all the data taken together, 16, 1·032, −1·269, 0·9817, 0·119. The Hammett σ-constants are:[2] *p*-NMe_2 (−0·600), *p*-OMe (−0·268), *p*-Me (−0·170), *p*-Cl (+0·227), and *p*-NO_2 (+0·778).

Ethylenediamine exists as the *gauche*-conformer in the gas phase.[6] Closing the imidazolidine ring brings the two nitrogen atoms closer. Theoretical calculations[7] and photoelectron spectra[8,9] have indicated a direct, through-space N · · · N interaction and a through-bond hyperconjugative effect[10] which can work in opposite directions in bridgehead diazabicycloalkanes. In molecules with two carbon bridges the through-bond mechanism is dominant. Replacing these by one-carbon bridges strengthens the through-space interaction.[7] Piperazine shows zero effect,[8] with the two mechanisms presumably in balance. In our imidazolidines one of the two-carbon bridges is replaced by E, bringing the two nitrogen atoms closer together for the through-space interaction which apparently predominates over all the other available mechanisms in each of the systems we have studied.

The E = CH_2 derivatives were synthesized by condensation of the *NN'*-unsymmetrically substituted ethylenediamine with formaldehyde,[11] the E = $SiMe_2$[1] and BPh derivatives by transamination, and the E = PPh[12] and P(O)Ph derivatives by amination. Addition of pyridine to solutions of the *N-p*-methoxyphenylboron derivative mixed with the reference *N-p*-nitrophenylboron compound broadened all the n.m.r. signals without changing the separation of the two dimethylamino resonances and gave rise to several new resonances with time. The separation of the two dimethylamino resonances in a similar mixture of the phosphorus imidazolidines did not change with temperature down to *ca.* −100 °C when viscosity broadening occurred.

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