The Elusive ($p \rightarrow d$)–π Bond

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WE have been led to take an agnostic view of supposed large ($p \rightarrow d$)–π contributions to the Si–, Ge–, and Sn–N bonds on the basis of n.m.r. experiments on the M–N–H skeleton. We have elsewhere pointed out that inconsistencies exist between the interpretation of $J(^{15}N–H)$ in such systems and the simple theory of ($p \rightarrow d$)–π interaction. Both the theory of spin–spin coupling and the postulate of ($p \rightarrow d$)–π interactions were treated with (and suffer from) the usual assumptions,[1,2] *e.g.*, it was stated that "the amount of *s*-character in the nitrogen hybrid should increase with ($p \rightarrow d$)–π bonding . . . since this interaction requires the use of a nitrogen orbital with large, perhaps pure, *p*-character."[1]

Dr. Ebsworth has since pointed out that there may be considerable overlap between a π-type *d*-orbital of silicon and a nitrogen lone pair which is

sp^3 in characeter, so that the steric situation at nitrogen is not necessarily an index of the occurence of $(p \rightarrow d)-\pi$ interaction.[3,4] This suggestion is a valuable revision of the view that a small amount of $(p \rightarrow d)-\pi$ bonding affects the geometry,[5,6] for if it can be supported by more detailed calculations of overlap, it would allow retention of the $(p \rightarrow d)-\pi$ hypothesis despite our results.[1] At the same time it weakens the predictive capacity of the theory for stereochemical purposes and magnifies the problem of explaining the force constant data.

The same kind of suggestion may be used with benefit for the discussion of $(p-p)-\pi$ interaction in substituted aromatics. Indeed, the idea is already implicit in investigations of $(p-p)-\pi$ interactions by dipole moments,[7] since the results of this method have been interpreted in terms not only of this interaction for the N–H group attached to a π-system, but also of a nonplanar arrangement of bonds about nitrogen.[8] This steric result for NH_2 has been recently confirmed in aniline, both by our n.m.r. studies[1] of [^{15}N]aniline and by microwave work.[9] The steric consequences of variation in the extent of $(p-p)-\pi$ interaction may be tested by investigation of substituted anilines. This is currently being done by n.m.r. studies on *p*-substituted anilines isotopically enriched in ^{15}N. The observed enhancement in $J(^{15}N-H)$ from 78 to 88 c./sec. for *p*-nitroaniline relative to aniline itself may be rationalized by increased $(p-p)-\pi$ interaction in the substituted compound leading to a flattening of the nitrogen pyramid.[10]

We find no such effect for trimethylgermyl-[11] and trimethylstannyl-[^{15}N]aniline, each of which has a $J(^{15}N-H)$ value very close to the values for trimethylsilyl[^{15}N]aniline, [^{15}N]aniline, and the [^{15}N]ammonium ion.[12] Thus, on the presupposition that $(p \rightarrow d)-\pi$ bonding occurs in these aniline derivatives, it is not *stereochemically* significant, as has already been remarked for the Ge–P bond in trigermylphosphine,[13] and as might also be remarked for $(Me_3Sn)_3X$ where X = N, P, As, and Sb.[14] There is, however, at the moment no need to make this presupposition at all! Indeed, the latest suggestion that planar skeletons such as Si_3N[5] and Si_3P[6,15] are characterized by large $(p \rightarrow d)-\pi$ interactions[3] is apparently contradicted by the view that the force constants for the Si–N and Si–P bonds depict single-bond character.[5,6] We may also note that the Sn–N bond is long and weak.[14] The situation allows no general solution.

One might hope to pursue the problem by nonstereochemical studies. Experiments designed to test the transmission of substituent effects through the silylamine system, however, fail to reveal any enhancement over directly analogous saturated organic systems.[16]

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[2] E. A. V. Ebsworth, "Volatile Silicon Compounds," Pergamon Press, London, 1963, p. 6.

[3] E. A. V. Ebsworth, *Chem. Comm.*, 1966, 530.

[4] Dr. Ebsworth challenges any assumption that the *occurrence* of this interaction is disproved by observation of a pyramidal situation at nitrogen, in say the Si–N case, but incorrectly attributes this assumption to reference 1. The argument there was concerned with the *extent* of the interaction which was never stated to be necessarily absent.

[5] E. A. V. Ebsworth, J. R. Hall, M. J. Mackillop, D. C. McKean, N. Sheppard, and L. A. Woodward, *Spectrochim. Acta*, 1958, **13**, 202.

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[7] A. R. Katritzky, E. W. Randall, and L. E. Sutton, *J. Chem. Soc.*, 1957, 1769, and references therein.

[8] R. J. B. Marsden and L. E. Sutton, *J. Chem. Soc.*, 1936, 599.

[9] D. G. Lister and J. K. Tyler, *Chem. Comm.*, 1966, 152.

[10] M. R. Bramwell and E. W. Randall, unpublished results.

[11] E. W. Randall, J. J. Ellner, and J. J. Zuckerman, unpublished results.

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[13] S. Cradock, G. Davidson, E. A. V. Ebsworth, and L. A. Woodward, *Chem. Comm.*, 1965, 515.

[14] R. E. Hester and K. Jones, *Chem. Comm.*, 1966, 317.

[15] G. Davidson, E. A. V. Ebsworth, G. M. Sheldrick, and L. A. Woodward, *Chem. Comm.*, 1965, 122.

[16] C. H. Yoder and J. J. Zuckerman, Abstracts 152nd A.C.S. Meeting, New York, N. Y., September, 1966; C. H. Yoder and J. J. Zuckerman, *Inorg. Chem.*, in the press.