## Note on the Charge-Transfer Band of the Pyridine–Iodine Complex[1]

Sir:

It is of interest that in the py $\cdot$ I_2 (pyridine $\cdot$ iodine) and related complexes, the donor should be able to function either as a π or as an n (lone-pair) donor. The fact that the py $\cdot$ I_2 complex in its normal state (as deduced from the solid 1:1 complex) is planar with the I_2 lying along the symmetry axis[2] shows that the stability of the complex results from n-donor action at the N atom. However, recent experimental[3] and theoretical[4] work make it fairly certain that the n I is at about 10.54 eV,[5,6] while the first π I is at 9.28 eV. The corresponding first π I in benzene is twofold degenerate, but in pyridine this degeneracy should be split to give two low π I's; in addition there should be, as in benzene, a third, higher, π I.

Even though the dative function interacting with the no-bond function to produce the stable complex is the one formed by removing a lone-pair electron for py, it is now necessary to ask whether transitions to CT (charge-transfer) states in which transfer to I_2 is from the π MO's of py make contributions to the observed CT spectrum. With axes chosen as in the structure given below, the observed π I at 9.28 eV should correspond to an MO (say π_y) nearly
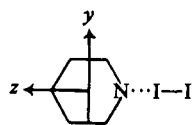
identical with the corresponding benzene MO, while the second π I (which possibly is close to the first, or perhaps is approximately coincident with the n I) involves participation of the N atom; this MO may be called π_z. The two corresponding CT states may be called $\pi_y^{-1} \sigma_u$ and $\pi_z^{-1} \sigma_u$ (σ_u represents the I_2^- MO into which the electron is transferred), while the CT state hitherto solely assumed to be involved may be called $n^{-1} \sigma_u$. A consideration of the selection rules for a complex of the symmetry shown in the structure shows at once that a transition to the CT state $\pi_y^{-1} \sigma_u$ is forbidden, while a transition to $\pi_z^{-1} \sigma_u$ is allowed with transition moment $e \int \pi_z x \sigma_u \, dv$ polarized in the x direction, that is, perpendicular to the plane of the complex. Further, in view of the strong overlap of the totally symmetrical functions π_z and σ_u, the transition moment integral should be large and the transition *strongly* allowed.

It is known[7] that the intensity of the py $\cdot$ I_2 CT band is

exceptionally high (ε_{max} 50,000, oscillator strength 1.12). Further, this band, although not unusually wide, is rather strongly asymmetric in an unusual way. Namely, although most CT bands spread more widely on the high-frequency than on the low-frequency side,[8] the py $\cdot$ I_2 band has v_L about 2900 cm^{-1} as compared with v_H about 2000 cm^{-1}.[9] (Here v_L is the difference between v_{max} and the low-frequency v at which ε has fallen to $^1/_2\varepsilon_{max}$, while v_H is the difference between the high-frequency v at which ε has fallen to $^1/_2\varepsilon_{max}$, and v_{max}.) The profile of the band can in fact be interpreted as having a slight bulge on the low-frequency side. This bulge can now be interpreted as corresponding to the $\pi_z^{-1} \sigma_u$ CT transition, and contributing to the otherwise anomalously high intensity observed for the $n^{-1} \sigma_u$ CT band.

(8) G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Göttingen, 1961.

(9) For comparison, the very strong CT band of $(C_2H_5)_3N \cdot I_2$ (S. Nagakura, *J. Am. Chem. Soc.*, **80**, 520, 1958) has v_L about 4000 cm^{-1} and v_H about 3500 cm^{-1}. (The kind of asymmetry here is also exceptional, but much less so than for the py $\cdot$ I_2 band.)

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Free-Radical Intermediates in a Benzyne Addition–Rearrangement Reaction

Sir:

The observation of chemically induced dynamic nuclear polarization (CIDNP) in the proton magnetic resonance (pmr) spectrum now allows us to deduce the rearrangement route for the benzyne adduct to N,N-dimethylbenzylamine. Enhanced absorption and stimulated emission for the α proton of the principal product, N-methyl-N-(α-phenethyl)aniline,[1] is indicative of a paramagnetic precursor.

Although benzyne generation by *n*-butyllithium attack on halobenzenes is normally too slow[2] to give the necessary concentration[3] of short-lived intermediate, addition of a small amount of the Lewis base N,N,N',N'-tetramethylethylenediamine (TMEDA) gave adequate rates for observation. Figure 1 shows pmr spectra for the reaction system, *n*-butyllithium in hexane (0.6 ml of 1.5 *M*, Foote Mineral), N,N-dimethylbenzylamine (0.25 ml),[4] TMEDA (6 μl),[5] and fluorobenzene (150 μl).[4] Addition of fluorobenzene to *n*-butyllithium–TMEDA gave very rapid evolution of a bright brown gas with a sweet choking odor; however the order of mixing other reagents was unimportant. Dimethylbenzylamine in *n*-butyllithium[6] gave a pink solution which changed to bright orange on

(1) This work was assisted by the Office of Naval Research, Physics Branch, under Contract No. N00014-67-A-0285-0001.

(2) See O. Hassel, *Mol. Phys.*, **1**, 241 (1958), for py $\cdot$ ICl. py $\cdot$ I_2 is no doubt similar.

(3) M. I. Al-Jaboury and D. W. Turner, *J. Chem. Soc.*, 4438 (1964), photoelectron spectroscopy; also *Tetrahedron Letters*, **35**, 3419 (1967).

(4) E. Clementi, *J. Chem. Phys.*, **46**, 4731, 4737 (1967); J. L. Whitten, *et al., ibid.*, **48**, 953 (1968); J. Del Benne and H. H. Jaffé, *ibid.*, **48**, 1811 (1968). All these calculations indicate that the first two π I's are smaller than the lone-pair I.

(5) This "lone-pair" I is really the lowest σ I and is not strictly N-atom lone pair. However (for reasons which are not evident qualitatively), the theoretical calculations[4] show it to be about 70% concentrated on the N atom, so that the "lone-pair" description is roughly correct.

(6) The identification of the I near 10.4 eV as n has also been concluded by M. A. El-Bayoumi and O. S. Khalil, *J. Chem. Phys.*, **47**, 4863 (1967).

(7) C. Reid and R. S. Mulliken, *J. Am. Chem. Soc.*, **76**, 3869 (1954), and see ref 1, Table 10-2.

(1) A. R. Lepley, 145th National Meeting of the American Chemical Society, New York, N. Y., Sept 1963, Abstracts, p 5Q.

(2) A. R. Lepley, R. H. Becker and A. G. Giumanini, unpublished work.

(3) R. G. Lawler, *J. Amer. Chem. Soc.*, **89**, 5519 (1967); J. Bargon and H. Fischer, *Z. Naturforsch.*, **22a**, 1556 (1967).

(4) Similar spectra but of different intensities were obtained when the amounts of these reagents were doubled.

(5) Amounts in excess of 10 μl gave reactions too vigorous for study.

(6) Metallation of the benzylic and *ortho* positions of the amine have been reported: W. H. Puterbaugh and C. R. Hauser, *J. Amer. Chem. Soc.*, **85**, 2467 (1963).