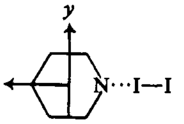
Note on the Charge-Transfer Band of the Pyridine–Iodine Complex[1]

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 ν_L about 2900 cm^{-1} as compared with ν_H about 2000 cm^{-1}.[9] (Here ν_L is the difference between ν_{max} and the low-frequency ν at which ε has fallen to $^1/_2\varepsilon_{max}$, while ν_H is the difference between the high-frequency ν at which ε has fallen to $^1/_2\varepsilon_{max}$, and ν_{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.

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(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.

(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 ν_L about 4000 cm^{-1} and ν_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.)

Robert S. Mulliken
Laboratory of Molecular Structure and Spectra
Department of Physics
University of Chicago, Chicago, Illinois 60637

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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

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(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.

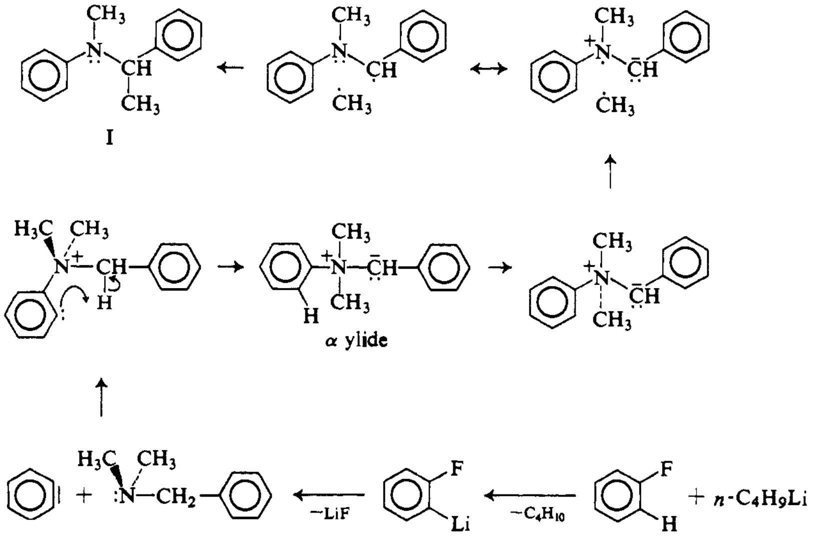
(3) R. G. Lawler, *J. Amer. Chem. Soc.*, **89**, 5519 (1967); J. Bargon and H. Fischer, *Z. Naturforsch.*, **22a**, 1556 (1967).

(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).

Scheme I



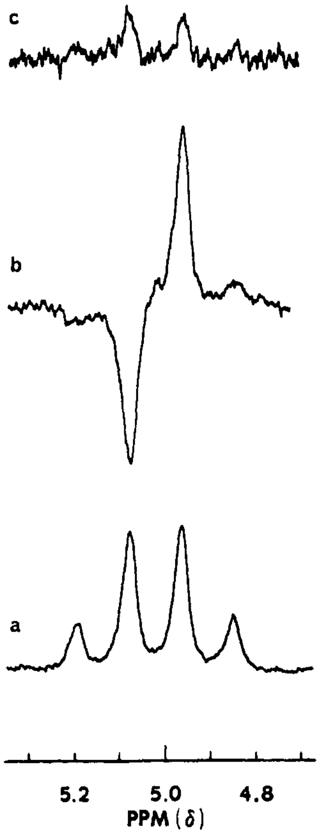


Figure 1. Proton magnetic resonance spectra in the range δ 5.4–4.6 ppm for (a) N-methyl-N-(α-phenethyl)aniline (∼5%) in 1:2:5 v/v fluorobenzene–N,N-dimethylbenzylamine–*n*-hexane; (b) and (c) 1-min scans started at 0.30 and 10 min after the addition of 150 μl of fluorobenzene to a mixture of 0.25 ml of N,N-dimethylbenzylamine, 6 μl of tetramethylethylenediamine, and 0.6 ml of 1.5 *M* *n*-butyllithium in hexane. The spectrum amplitude for scans b and c was 80 on a Varian A-60A spectrometer.

addition of TMEDA, but no major change in the CH_2Li pmr band location,[7] δ −0.83 ppm, was observed. The emission–absorption quartet at δ 5.02 ppm (Figure 1b) built up in 2–3 min and then rapidly decreased, giving the weak absorption spectrum in Figure 1c after 10 min.[8]

The location of this emission–absorption band was identical with that of the quartet (Figure 1a) from the benzylic methine proton in N-methyl-N-(α-phenethyl)-aniline (I) which was synthesized[2] from α-bromoethylbenzene and N-methylaniline. The benzyne–amine addition and rearrangement system studied here gave a 33% yield of I in anhydrous ether.[1,10]

Since CIDNP has only been observed for species which come from free-radical-generating reagents directly[11] or by radical transfer,[9] the final product has a free-radical intermediate as a direct precursor. Scheme I depicts a route in which a radical pair gives rise to the product, I. This radical pair is basically a specific type of representation for a 1,2 shift in the Stevens rearrangement but must have sufficient electron unpairing so that electron paramagnetism can cause the observable nuclear polarization. The conjugation and associated resonance forms for electron delocalization in the aromatic member may aid in lowering the energy barrier for formation of this pair. Selective proton migration in the benzyne adduct, an *o*-betaine, gives the α ylide from which the free-radical pair is formed.

The rearrangement is effectively an internal nucleophilic displacement. However the dissociation of, and recombination with, the methyl radical involves what is essentially a one-electron-transfer process. Recent electron spin resonance experiments have given rise to the suggestion[12] that similar two-step, one-electron processes are involved in classical S_N1-type heterolytic reactions.

An alternative description of the migration invokes one-electron transfer from the α ylide to and from some second reagent, *e.g.*, butyllithium or benzyne. Loss of an

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(7) *Cf.* T. L. Brown, *Advan. Organometal. Chem.*, **3**, 365 (1965).

(8) The region δ 10 to −2 ppm was scanned, but no additional emission bands were observed. Aromatic and aliphatic CH regions, containing the CH_3 adjacent to methine in the product, were obscured by solvent and reactant absorptions. TMS was used as an internal calibration standard in most experiments. Polarization of other alkyl groups on the nitrogen attached to the paramagnetic site has not been observed; *cf.* ref 9.

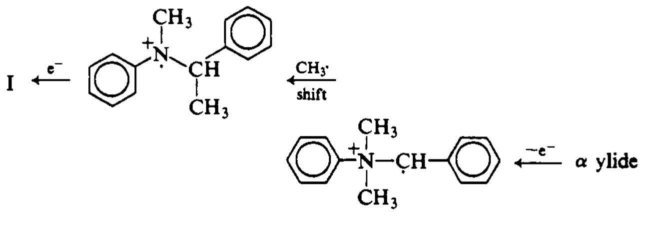
(9) A. R. Lepley, *J. Amer. Chem. Soc.*, 90, 2710 (1968).

(10) Less than 0.5% of any other rearrangement product was observed.[2] H. Hellmann and W. Unseld, *Ann.*, **631**, 82 (1960), have obtained I in an analogous benzyne reaction.

(11) H. R. Ward and R. G. Lawler, *J. Amer. Chem. Soc.*, **89**, 5518 (1967); J. Bargon, H. Fischer, and U. Johnsen, *Z. Naturforsch.*, **22a**, 1551 (1967).

(12) K. A. Bilevitch, N. N. Pubnov and O. Yu. Okhlobystin, *Tetrahedron Letters*, 3465 (1968).

electron from the ylide gives a radical cation which methyl radical shift (methyl carbonium ion shift requires a one-electron C–C bond in the final intermediate) converts to an anilinyl cation. An electron must then be regained to reach I. If nuclear polarization is to be observed in this case, the last two steps must be much faster than the nuclear spin relaxation time[13] or a strong polarization of the group adjacent to the final unpaired electron site is required. But extended CIDNP has only been observed during intense polarization activity.[14] Furthermore the bimolecularity and less extensive resonance interactions for intermediates along this rearrangement route decrease its viability.



The intensity of the observed pmr effect requires that a free-radical intermediate be a direct product precursor. In addition, the particular form of the observed spectrum indicates that the major variations in spin state populations are for the most probable transitions.[15] Thus a closely associated and short-lived free-radical pair as in Scheme I may be reasonable.

(13) K. H. Hausser and D. Stehlik, *Advan. Magnetic Resonance*, **3**, 79 (1967).

(14) A. R. Lepley, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, Abstract PHYS-109.

(15) A —1:—1:1:1 pattern might otherwise be anticipated.[14]

Arthur R. Lepley
Department of Chemistry, Marshall University
Huntington, West Virginia 25701

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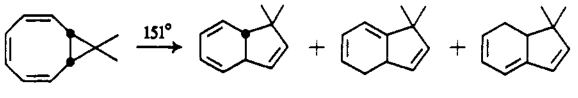
On the Mechanism of the Thermal Reorganization of Bicyclo[6.1.0]nona-2,4,6-trienes to 8,9-Dihydroindenes

Sir:

Since the first report of the title reaction 8 years ago, many additional examples have been published.[1,2] A number of workers have considered possible mechanisms, the greatest amount of attention having been focused on the hypothetical intermediacy of 1,3,5,7-cyclononatetraene or derivatives thereof.[1a-d,f,h,3] The problem which arises with this mechanism is that concerted ring opening and closing are predicted[4] to proceed *via* a *cis,cis,cis,trans*-1,3,5,7-cyclononatetraene to give the corresponding *trans*-8,9-dihydroindene, whereas a *cis*-8,9-dihydroindene has been found to be the major product in every case in which the stereochemistry at the ring fusion has been established.[1a-e,h] In an attempt to overcome this difficulty it has recently been suggested that an all-*cis* cyclononatetraene is formed as an intermediate in a step in which orbital symmetry is not conserved.[3c]

In order to elucidate the steric requirements of this reaction we have synthesized 9,9-dimethylbicyclo[6.1.0]-nona-2,4,6-triene (**1**). This was accomplished in 88% yield by the addition of a solution of 2,2-dichloropropane in ether to lithium cyclooctatetraene dianion in liquid ammonia at *ca.* −33°.[5] The structure of the product follows from its typical *cis*-fused bicyclo[6.1.0]nona-2,4,6-triene uv spectrum[1e,6] ($\lambda_{\max}^{\text{hexane}}$ 248 mμ (ε 3710)) and the nmr spectrum.[7,8]

When **1** is heated at 151° (0.05 *M* in refluxing nonane) for 15.0 min the reaction mixture consists of 87% **1** and 12% **2** along with two minor components (**3** and **4**); after 60.0 min the mixture contains 53% **1**, 25% **2**, 8% **3**, 13% **4**, and a fourth unidentified product (1%). Products **2**, **3**, and **4** are isomers; the latter two were shown to arise from **2** and are themselves reasonably stable under the reaction conditions.



1 **2** **3** **4**

Isomer **2** was identified as *trans*-1,1-dimethyl-8,9-dihydroindene on the basis of its uv ($\lambda_{\max}^{\text{hexane}}$ 259.5 mμ (ε 3300))[9a] and nmr (multiplet at τ 3.6–4.5 (6 H, vinyl), AB quartet at 6.88 (2 H, bridgehead, J_{AB} = 20 Hz),[10] singlets at 8.87 and 9.06 (3 H each, methyl)) spectra and catalytic hydrogenation (3 mol equiv) to *trans*-1,1-dimethylhydrindan. Isomers **3** and **4** were assigned the structures indicated primarily on the basis of their uv ($\lambda_{\max}^{\text{hexane}}$ 265.5 (ε 4700) and 302 mμ (9870), respectively)[9] and nmr spectra.[11] Each was catalytically hydrogenated (3 mol equiv) to give *cis*-1,1-dimethylhydrindan as the major product.

The formation of **3** and **4** from **2** can be explained by

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(1) (a) E. Vogel and H. Kiefer, *Angew. Chem.*, **73**, 548 (1961); (b) E. Vogel, W. Wiedemann, H. Kiefer, and W. F. Harrison, *Tetrahedron Lett.*, 673 (1963); (c) K. F. Bangert and V. Boekelheide, *Chem. Ind.* (London), 1121 (1963); *J. Am. Chem. Soc.*, **86**, 905 (1964); (d) G. J. Fonken and W. Moran, *Chem. Ind.* (London), 1841 (1963); (e) T. J. Katz and P. J. Garratt, *J. Am. Chem. Soc.*, **85**, 2852 (1963); **86**, 5194 (1964); (f) E. A. LaLancette and R. E. Benson, *ibid.*, **87**, 1941 (1965); (g) T. L. Burkoth, *J. Org. Chem.*, **31**, 4259 (1966); (h) W. Grimme, *Chem. Ber.*, **100**, 113 (1967).

(2) (a) An 8,9-dihydroindene has been proposed as an intermediate but was not isolated: T. S. Cantrell and H. Shechter, *J. Am. Chem. Soc.*, **89**, 5868 (1967). (b) It is likely that bicyclo[6.1.0]nona-2,4,6-triene is an intermediate in the pyrolysis of *cis*-bicyclo[5.2.0]nona-2,4,8-triene to *cis*-8,9-dihydroindene: M. Jones, Jr., and S. D. Reich, *ibid.*, **89**, 3935 (1967).

(3) (a) E. Vogel, *Angew. Chem. Intern. Ed. Engl.*, **2**, 1 (1963); (b) A. G. Anastassiou, *J. Am. Chem. Soc.*, **90**, 1527 (1968); (c) J. M. Holovka, P. D. Gardner, C. B. Strow, M. L. Hill, and T. V. Van Anken, *ibid.*, **90**, 5041 (1968).

(4) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968), and references cited therein.

(5) Unsubstituted and *syn*-9-methylbicyclo[6.1.0]nona-2,4,6-triene and bicyclo[6.2.0]nona-2,4,6-triene have also been prepared by this procedure. It affords higher yields (60–90%) and is generally faster (4–5-hr stirring) and more convenient than other methods.[1a,b,e]

(6) G. Moshuk, G. Petrowski, and S. Winstein, *J. Am. Chem. Soc.*, **90**, 2179 (1968).

(7) The nmr spectrum displays a multiplet centered at τ 4.2 (6 H, vinyl), a singlet at 8.80 (5 H, *anti*-methyl and cyclopropyl), and a singlet at 9.04 (3 H, *syn*-methyl). *Cf.* the spectrum of *syn*-9-methylbicyclo[6.1.0]nona-2,4,6-triene.[1e]

(8) All new compounds have been fully characterized and gave satisfactory elemental analyses.

(9) (a) This value of $\lambda_{\max}$ is very similar to those of *cis*-8,9-dihydroindene[1e] and its derivatives.[1c,e,f] (b) *Cf.* $\Delta^{2,4,6}$-22-Isospirostatriene ($\lambda_{\max}$ 306 mμ (ε 21,000)): J. Romo, H. J. Ringold, G. Rosenkranz, and C. Djerassi, *J. Org. Chem.*, **16**, 1873 (1951).

(10) *cis*-8,9-Dihydroindene has J_{AB} = 12 Hz for the bridgehead protons.

(11) Each isomer has five vinyl and six methyl protons; **3** has one diallylic and two allylic protons whereas 4 has three allylic protons.