Table I. Catalysis of HD Exchange by Metal Hydrides[a]

					Gas analysis					
					Theory[b]			Found		
Expt	Complex (mmol)	Solvent	Gas (mmol)	Temp, °C	H_2	HD	D_2	H_2	HD	D_2
A	I (0.16)	C_6D_6	H_2 (0.15)	100				41.4	41.6	17.0
B	II (0.11)	C_6H_6	D_2 (0.08)	25	74.1	24.0	1.9 (9)	72.6	24.8	2.6
C	II (0.11)	C_6H_6	D_2 (0.08)	100	92.2	7.7	0.15 (35)	98.5	1.5	
D	II (0.095)	C_6D_6	H_2 (0.46)	100				10	38	52
E[c]	II (0.095)	C_7H_8	D_2 (0.49)	100	21.7	49.8	28.5 (9)	62.5	32	5.6
F	(PhPEt₂)₃IrH₃ (0.093)	C_6H_6	D_2 (0.49)	100	4.84	34.3	60.8 (3)	8.8	38	53.2
					21.0	49.7	29.3 (9)			

[a] These experiments were carried out in sealed glass ampoules of 4- or 15-ml capacity to give an H_2 or D_2 pressure of about 1 atm. The amount of solvent used in each was 2 ml, and the standard heating period was 24 hr. [b] Calculated for statistical exchange of D_2 with the number of ligand hydrogen atoms per molecule indicated in parentheses. [c] Mass spectrum of the toluene indicates *ca.* 1% toluene-d_1 over the natural abundance.

undergoes exchange of metal–hydrogen with C_6D_6. However, the interaction we have observed is more complex than that reported for the rhenium hydride. When a C_6D_6 solution of I is heated under a hydrogen atmosphere, HD and D_2 appear in the vapor phase (Table I, experiment A). Under these conditions, deuterium could only come from the solvent. Its presence definitely indicates catalytic exchange.

Similar catalysis of exchange between H_2 and C_6D_6 or between D_2 and C_6H_6 was observed with the iridium hydrides II,[6] III,[6] and IV.[7] Exposure of a C_6H_6 solution of II[6] to D_2 for 24 hr at 25° results in statistical exchange of nine hydrogens per molecule of iridium complex (experiment B), a value which corresponds to reaction of the five Ir–H and four *o*-C–H bonds. However at 100° more H_2 and HD were present in the gas phase than could be accounted for even if every hydrogen in the complex equilibrated with the gas phase (experiment C). As with $(C_5H_5)_2TaH_3$, the inverse experiment in deuteriobenzene with H_2 as the exchanging gas gave a substantial amount of HD and D_2 after 24 hr at 100° (experiment D). Exchange with solvent also occurs with toluene (experiment E). The six-coordinate complex *mer*-$(PhPEt_2)_3IrH_3$[6] exchanges slightly more than three hydrogens after 24 hr at 100°, a substantial decline in activity for ligand exchange (experiment F).

In benzene solution the iridium hydrides II–IV decompose spontaneously with evolution of hydrogen, but no metal is deposited.[8] When I is heated under N_2 in benzene at 80° for 15 hr, H_2 is detected in the gas phase. Heating I in benzene with excess Et_3P produces a red crystalline solid whose nmr spectrum[9] indicates that it should be formulated as $(\pi\text{-}C_5H_5)_2Ta(H)PEt_3$.

The conversion to the new product is low in a sealed tube but is complete under a N_2 sweep in refluxing toluene. This result suggests that an equilibrium exists between the phosphine hydride and the trihydride. This new complex also catalyzes the exchange of D_2 with benzene. The thermal evolution of hydrogen from these complexes coupled with the exchange data suggest the existence of the equilibria illustrated for the tantalum complex.
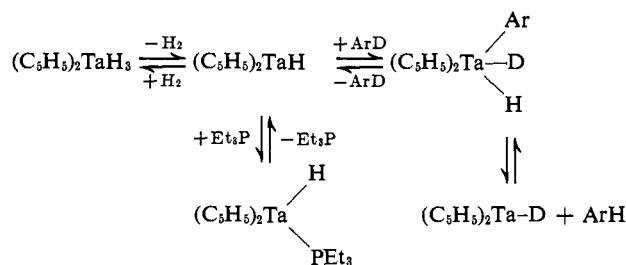
Similar equilibria are presumed to occur with the iridium hydrides.

No evidence is presently available concerning the intermediate formed by oxidative addition of an aromatic C–H bond. Aryl hydride complexes have been reported,[10] and a tautomerism between $Ru(dmpe)_2$-$C_{10}H_8$ and $HRu(dmpe)_2C_{10}H_7$ (dmpe = bis-1,2-dimethylphosphinoethane) was observed.[10] Garnett and Hodges[2] have also postulated an analogous addition product in their exchange mechanism. Such an intermediate could have great importance, for it provides an aromatic ring which is susceptible to electrophilic substitution.

(5) J. Chatt and R. S. Coffey, *J. Chem. Soc. A*, 1963 (1969).

(6) B. E. Mann, C. Masters, and B. L. Shaw, *Chem. Commun.*, 703 (1970).

(7) Prepared by LiAlH₄ reduction of Me₃PH⁺[IrCl₄(Me₃P)₂]⁻ in THF and isolated by sublimation from the residue which remains after evaporation of solvent from the hydrolysate. The ¹H nmr spectrum in toluene consists of two triplets in the rato 18:5.5 at τ 8.26 (J_{P-CH_3} = 4 Hz) and 19.73 (J_{P-IrH} = 14 Hz). The ³¹P nmr consists of a symmetrical sextet (0.94:5:10) at +192.1 ppm from external trimethyl phosphite. The infrared spectrum shows a strong broad absorption at 1920 cm⁻¹ for ν_{IrH}.

(8) A number of new hydride resonances are observed in the nmr spectra of these solutions after decomposition. The compositions of these products are being studied.

(9) The proton nmr spectrum in C_6D_6 at 220 MHz shows cyclopentadienyl absorption at τ 5.68 as a doublet of doublets (J_{PH} = 1.7, J_{HH} = 0.5 Hz), a five-line CH₂ signal (overlapping quartets, J_{PH} = 7, J_{HH} = 7.5 Hz) at τ 8.91, a five-line CH₃ signal (overlapping triplets, J_{PH} = 13.5 Hz) at τ 9.16, and TaH absorption at τ 19.48 (J_{PH} = 21 Hz). The relative intensity ratio C_5H_5:C_2H_5:TaH is 10:15.5:0.9.

(10) J. Chatt and J. M. Davidson, *J. Chem. Soc.*, 843 (1965).

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Electron Spin Resonance Study of Dialkylamino Free Radicals in Solution[1]

Sir:

It is generally accepted that the most stable conformation of simple alkyl free radicals is a planar, sp^2 hybridized form with the unpaired electron located in
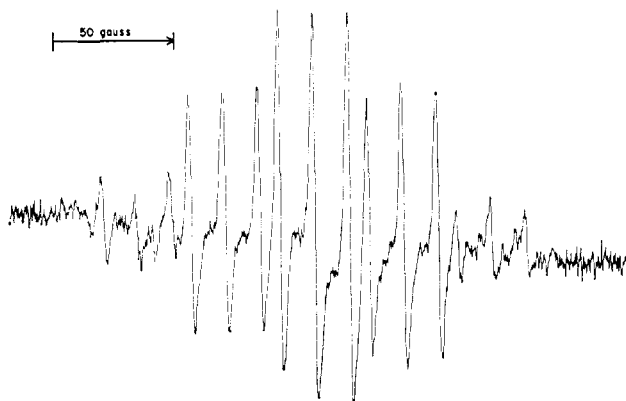
Figure 1. Electron spin resonance spectrum of diethylamino radical in cyclopropane solution at $-90 \pm 2°$.

the p orbital while ammonia and aliphatic amines possess a rapidly inverting pyramidal structure with the lone pair of electrons in a more-or-less sp^3 hybridized orbital.[2] The dialkylamino free radicals would thus appear to be an electronically unique type of radical species in which the central atom must accommodate both lone-pair electrons and an unpaired electron. The rather large isotropic nitrogen hyperfine interaction of 32 G reported by Hadley and Volman[3] for both methylamino and dimethylamino free radicals would suggest that the unpaired electron resides in a hybrid orbital with appreciable s character. We presently wish to report the high-resolution electron spin resonance (esr) spectra of dimethyl-, diethyl-, and diisopropylamino radicals in solution which indicate that the isotropic nitrogen hyperfine coupling constant is in fact less than one-half the earlier reported value, signifying that the unpaired electron resides primarily in the nitrogen 2p orbital (1). Analysis of

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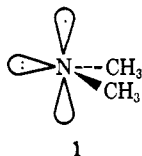
the β-hydrogen hyperfine interactions also reveals decided conformational preferences in the diethylamino and diisopropylamino radicals.

The amino radicals were generated from the corresponding tetrazenes[4] by photolysis[5] directly in the cavity of the esr spectrometer according to the elegant method recently developed by Kochi and Krusic.[6]

$$R_2N{-}N{=}N{-}NR_2 \xrightarrow{h\nu} 2R_2N\cdot + N_2$$
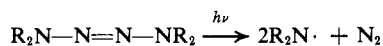
A *ca.* 10% solution of the tetrazene in cyclopropane gave a sufficiently high steady-state concentration of the corresponding dialkylamino radical to allow well-resolved esr spectra to be recorded (Figure 1); higher

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(3) S. G. Hadley and D. H. Volman, *J. Amer. Chem. Soc.*, 89, 1053 (1967).

(4) W. R. McBride and W. E. Thun, *Inorg. Chem.*, 5, 1846 (1966).

(5) A PEK A-1-B, 2000-W, high-pressure mercury capillary lamp was utilized in conjunction with a spherical reflecting mirror and a suitable lens system.

(6) J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, 91, 6161 (1969).

initial concentrations of tetrazene produced a mixture of radicals presumably formed by hydrogen abstraction of the labile hydrogens of either the undecomposed tetrazene or reaction products. A substantially stronger esr signal was obtained with the diisopropylamino radical which allowed the spectrum to be recorded over a range of temperatures. Results are listed in Table I.

Table I. Hyperfine Splitting Constants of Dialkylamino Radicals Produced by Irradiation of the Corresponding Tetrazenes[a]

Radical	a^N	a_β^H	a_γ^H
$(CH_3)_2N\cdot$	14.7_8	27.3_6	
$(CH_3CH_2)_2N\cdot$	14.2_7	36.9_0	b
$[(CH_3)_2CH]_2N\cdot$	14.3_1	14.3_1	0.6_6

[a] All spectra in cyclopropane solution at $-90 \pm 2°$ *vs.* Fremy's salt taken as 13.091 G (R. J. Faber and G. K. Fraenkel, *J. Chem. Phys.*, 47, 2462 (1967)); estimated accuracy $\pm 1.0\%$. [b] Not resolved.

It can be seen from the data that the isotropic nitrogen hyperfine interaction is on the order of 14 G indicating that the unpaired electron is located predominantly in the nitrogen 2p orbital (1) since the nitrogen coupling would be much larger for unpaired electron residence in an sp^3 or other hybrid orbital.[7-9] INDO calculations[10] for dimethylamino free radical indicate that there is a spin density of *ca.* 0.85 in the nitrogen 2p orbital and only 0.039 in the nitrogen 2s orbital. The calculations predict nitrogen and hydrogen hyperfine coupling constants of 14.80 and 26.69 G, respectively, for a CNC bond angle of 127° and a C–N bond distance of 1.40 Å.[11] The calculated nitrogen hyperfine interaction is quite dependent upon the CNC bond angle and it is encouraging to see that the INDO calculations, although by no means conclusive, suggest an equilibrium bond angle greater than 120° indicating that methyl–methyl repulsions are greater than methyl–lone pair repulsions. Similar effects are noted in dimethylamine where the CNC angle is known to be 112° 38' which is slightly greater than the idealized tetrahedral angle.[12]

It can be seen from the data in Table I that the magnitudes of the β-hydrogen hyperfine coupling constants for the three radicals are quite different with the diethylamino exhibiting a significantly larger interaction than dimethylamino while the coupling in diisopropylamino is considerably smaller. If one assumes the usual $\cos^2\theta$ relationship[13] correlating the

(7) W. M. Tolles, D. W. Moore, and W. E. Thun, *ibid.*, 88, 3476 (1966).

(8) T. Cole, *J. Chem. Phys.*, 35, 1169 (1961).

(9) G. Cauquis, M. Genies, H. Lemaire, A. Rassat, and J. P. Ravet, *ibid.*, 47, 4642 (1967).

(10) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Amer. Chem. Soc.*, 90, 4201 (1968). A copy of this program was obtained from the Quantum Chemistry Program Exchange, Indiana University, No. 141.

(11) The INDO calculations are complicated by the fact that the exact structure of the radical is not known. The 1.40-Å C–N bond length is somewhat shorter than the 1.46 Å found for dimethylamine but a probably more significant structural effect is that the axes of the methyl groups in dimethylamine are not collinear with the C–N bond but rather the methyl hydrogens are tilted up toward the lone-pair orbital of the nitrogen atom.[12] These conformation effects as related to the INDO calculations on the dimethylamino radical will be discussed at length in the detailed publication of this work.

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(13) D. H. Geske, *Progr. Phys. Org. Chem.*, 4, 125 (1967).

magnitude of the β-hydrogen coupling constant with the angle θ between the C–H bond and the axis of the p orbital containing the unpaired electron it is possible to estimate θ for the time-averaged equilibrium conformations of diethylamino and diisopropylamino radicals as 35 and 60°, respectively. It is obvious from an examination of molecular models that the rather decided conformational preferences in these radicals arise from steric interactions of the alkyl groups. These effects are minimized in diethylamino radical when the C–C bond of each ethyl group lies approximately in the nodal plane of the nitrogen p orbital (2) and in diisopropylamino radical when the C–H bond approaches to within about 35° of the nodal plane (3).
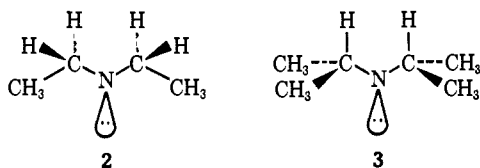
The spectrum of the latter species was observed to be almost invariant over a 150° temperature range (-120 to $+30°$). Although the fortuitous near equivalence of the nitrogen and hydrogen hyperfine coupling constants complicated by the hyperfine interaction of the twelve γ-hydrogens precluded an exact assessment of the β-hyperfine coupling constant, it appears that there is a change of less than 0.5 G over the temperature range investigated.

No evidence was observed under our photolytic conditions for any transformations involving hydrogen migration in these dialkylamino free radicals.[14,15]

We are presently investigating a wide variety of neutral amino free radicals in solution.

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Nuclear Magnetic Resonance Spectrum of Oriented Bullvalene

Sir:

It is well known that valence-bond isomerization can have a striking effect on the isotropic nmr spectra of fluxional molecules;[1] line shapes and splittings depend on the rate of the isomerization *vis-à-vis* the difference in resonant frequencies of individual structures. Similarly, when a static (*i.e.*, nonisomerizing) molecule is

(1) W. von E. Doering and W. R. Roth, *Angew. Chem., Int. Ed. Engl.*, 2, 115 (1963); G. Schroder, M. Oth, and R. Merenyi, *ibid.*, 4, 752 (1965).
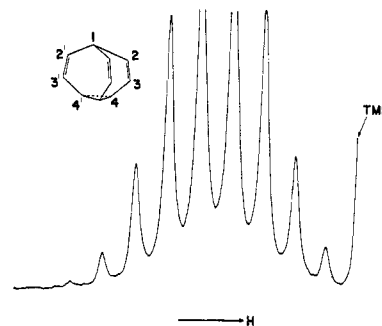

Figure 1. ^{1}H nmr spectrum of bullvalene oriented in a nematic liquid crystal solvent at 130°, read out after 60 runs on a C-1024 computer of average transients. The spectrum was read out at high gain to show up the downfield line; as a result, the two most intense lines are off the chart paper.

partially oriented in the anisotropic environment of a liquid crystal solvent, the spectral characteristics are influenced by the rate of exchange among ordered and disordered sites relative to the difference in resonant frequencies of molecules in these sites.[2] If the two situations are combined, and a fluxional molecule is dissolved in a liquid crystal solvent, all three processes are competitive, and a fourth, the rate of reorientation of the solute molecule in an ordered site, may enter if isomerization disturbs the local ordering. A dramatic example is provided by a nematic solution of bullvalene (tricyclo[3.3.2.0^{4,6}]deca-2,7,9-triene).[1] The purpose of this communication is to report the nmr spectrum of oriented bullvalene, and the ordering parameter[3] of the static molecule.

A 30 mol % solution of bullvalene in *p*-bis(heptyloxybenzoyloxy)benzene containing a few drops of TMS was degassed and sealed; the nematic range of this solution is 112–174°. The ^{1}H nmr spectrum at 130°, shown in Figure 1, is a symmetrical ten-line multiplet with 54-Hz spacing. The width of the lines (20 Hz) is about five times that normally observed in nematic solutions, and intensity measurements are unreliable because of the overlap. Nevertheless, the spectrum is unmistakably characteristic of an oriented system of ten magnetically equivalent spin-$\frac{1}{2}$ nuclei.[4] The separation between lines is three times the coupling constant, and intensities are in the ratio of the binomial coefficients of order ten.

The following mechanism is proposed to explain how the magnetic equivalence arises. Bullvalene orients in a configuration of minimum energy dictated by its shape and by dispersion forces.[5] The lifetime of a valence isomer at 130° is 10^{-6} sec,[6] and the exchange rate among sites ($>10^7$ sec^{-1})[2,7] ensures that the molecule will not isomerize at every site. Therefore, bullvalene orients like a static molecule between isomerizations; however, when a rearrangement does occur, the molecule is forced into an energetically unfavorable configuration and must reorient. A rough estimate of the reorientation rate is 10^{10} sec^{-1}; this was obtained by as-

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(5) A. Saupe, *Mol. Cryst.*, 1, 527 (1966); J. Nehring and A. Saupe, *Mol. Cryst. Liquid Cryst.*, 8, 403 (1969).
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(7) W. A. Hoyer and A. W. Nolle, *J. Chem. Phys.*, 24, 803 (1956).