HINDERED ROTATION ABOUT THE CARBON-NITROGEN SINGLE BOND IN N'-ARYL-N,N-DIMETHYLFORMAMIDINES

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Recently a communication appeared in this Journal concerning "a novel solvent effect in the nmr spectra of N,N-dimethylformamidines"[1] which deserves further comment. Examination of the data presented by the authors of the above-mentioned communication indicates that they have failed to differentiate between two unrelated pheonomena which led them to misleading conclusions. This fact can best be demonstrated by data of our own which serves to clarify the matter.

As can be seen from fig. 1 N'-aryl-N,N-dimethylformamidines exhibit typical temperature dependent nmr spectra which are usually associated with hindered rotation, as observed in related systems.[2] For example, the nmr spectra of N'-(p-nitrophenyl)-N,N-dimethylformamidine (I) at various temperatures (fig. 1) exhibits a typical coalescence sequence attributable to the equilibrium Ia⇌Ib. This rotational barrier is readily attributable to the additional π-bonding arrising from dipolar resonance contributors such as in Ic in the ground state. This rate process is observable in both chloroform and benzene solution, which was not recognized by Marsh

| Ia | Ib | Ic |
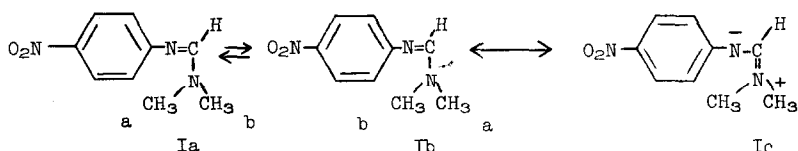
and Goodman. The source of this confusion is simply the fact that these solvents affect the relative chemical shifts which change the $\Delta\nu$ term in the rate expression[3] and thus the coalescence temperature. Therefore, in the nmr spectrum of compound I in c..oroform solution, $\Delta\nu$ is small enough that the coalescence temperature is below ambient. However, in benzene solution the $\Delta\nu$ term is large due to some solvent-solute interaction as observed in related systems,[4] and the coalescence temperature is above ambient and the methyl signals are resolved.

FIG: I
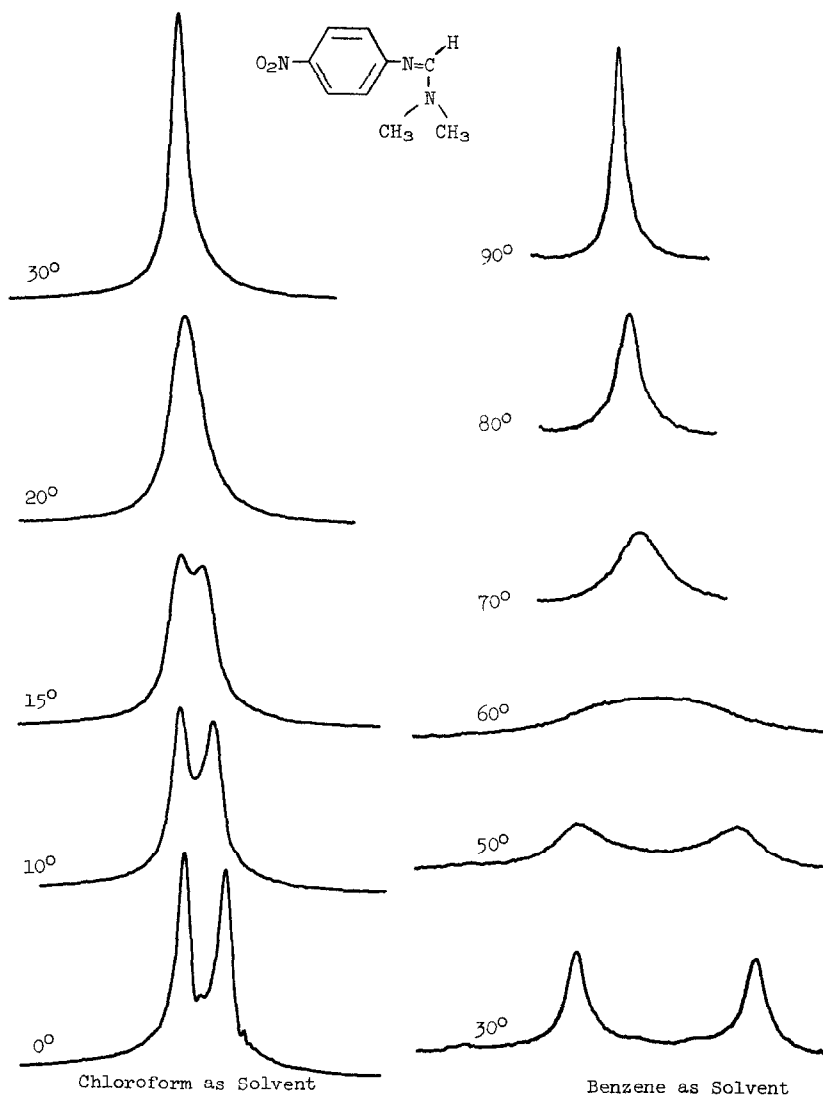
NMR Coalescence Spectra for N'-(p-nitrophenyl)-N,N-dimethylformamidine

The nmr spectra of N'-(p-tolyl)-N,N-dimethylformamidine at various temperatures exhibits

curves essentially identical to those shown in fig. 1 in the same solvent except that the

coalescence temperatures are lower. The rates of rotation at each temperature can be estimated

and used to calculate the activation parameters listed in Table 1. These data serve to empha-

size that for the type of processes being observed here, no sound conclusion can be drawn from

only ambient temperature nmr spectra. Thus, in benzene solution at lower temperatures the

broad singlet observed at ambient temperature for the N-methyl signal of N'-(p-tolyl)-N,N-dimeth-

ylformamidine separates into two signals separated by 51.5 cps. Also, by cooling chloroform

solutions, the nmr singlet for the N-methyl groups separates into two approximately equal sig-

nals separated by 4.7 cps. The temperature dependence of the nmr spectra of these compounds

as reported by Marsh and Goodman cannot be attributed to complex formation between benzene and

the formamidine system since it is also observed in chloroform (and several other solvents).

TABLE 1[*]

Compound[(5)]	Conc.	Solvent	$\Delta\nu$	ΔF Kcal	ΔH[(6)] Kcal	ΔS e.u.
N'-(p-nitrophenyl)-N,N-di-methylformamidine (I)	0.1 molal	$CHCl_3$	4.7	15.9 ± .3	10.3 ± .7	-20 ± 3
"	"	C_6H_6	42.5	15.2 ± .6	22.2 ±1.0	+21 ± 3
N'-(p-tolyl)-N,N-dimethyl-formamidine	"	$CHCl_3$	4.7	14.1 ± .2	12.1 ± .3	-8 ± 1
	"	C_6H_6	51.5	13.9 ± .2	12.6 ±1.3	-4 ± 3

* The spectra were determined at 100 MHz, with a Varian Associates HA-100 instrument. The solvent resonance was used to provide a lock signal. Temperatures were maintained with the V-6040 controller and were calibrated with the standard samples of methanol and ethylene glycol supplied by Varian. Rate constants in benzene were estimated by application of the various limiting forms of the Gutowsky-Holm equation.[(6)] Because of considerable overlap of the signals, the rate constants in chloroform were determined by comparing computer-generated line-shapes to the experimental curves. A FORTRAN IV program based on the complete Gutowsky-Holm equation was used to generate these theoretical line-shapes.

The activation parameters calculated for these processes are interesting and point out

that Marsh and Goodman were partially correct in assigning some unusual benzene-substrate com-

plex in some cases. The data for N'-(p-tolyl)-N,N-dimethylformamidine indicate essentially

identical activation parameters for both solvents indicating that benzene does not effect the

relative stabilities of the ground state or transition state in any way dissimilar from chloro-

form for this compound. However, the activation parameters for N'-(p-nitrophenyl)-N,N-dimethyl-

formamidine are quite different in the two solvents. The relatively larger enthalpy and the

large positive entropy of activation for rotation about the carbon-nitrogen single bond of

N'-(p-nitrophenyl)-N,N-dimethylformamidine in benzene indicates that the solvent may very well

stabilize the ground state by some specific interaction (possibly with the nitro group) which

is relaxed in the transition state.

Finally, it is worth noting that the benzene-solute interaction which causes the rela-

tively large Δν effect in the nmr spectra of these compounds need not necessarily be related

to the same interaction in the p-nitro system which causes the solvent effect on the activation

parameters. Thus the Δν effect for the p-tolyl system is larger than that for the p-nitro

compound which is directly opposite to the solvent effect on activation parameters.

Work is presently in progress to further establish the nature of the various factors

which determine the magnitude of the chemical shift differences and the barrier to rotation in

these systems.

<div align="center">References</div>

1   J. P. Marsh, Jr. and L. Goodman, Tetrahedron Letters, No. 8, 683 (1967).
2   H. S. Gutowsky and C. H. Holm, J. Chem. Phys., 25, 1228 (1956); W. D. Phillips, J. Chem.
    Phys., 23, 1363 (1955); M. T. Rogers and J. C. Woodbrey, J. Phys. Chem., 66, 540 (1962).
3   J. W. Emsley, J. Feeney and L. H. Sutcliffee, High Resolution Nuclear Magnetic Resonance,
    Pergamon Press, London, 1965, pp. 550-560.
4   Reference 3, pp. 841-860.
5   The compounds were prepared by the procedure described by H. Bredereck, R. Compper,
    K. Klemm and H. Rempfer, Ber., 92, 837 (1959).
6   Reference 3, pp. 485-488. The frequency of the coalesced peak varied ca. 10% from the
    mean frequency of the two low temperature signals. Since it would not be expected that
    the chemical shift difference Δν would vary more than this amount, the error introduced
    in ΔH* and ΔS* would not significantly effect the conclusions in the text.

<div align="center">Acknowledgement</div>