

TEMPERATURE DEPENDENCE OF THE C-METHYL CHEMICAL SHIFTS

IN N-SUBSTITUTED HYDRAZONES OF ACETONE

C.I. Stassinopoulou, C. Zioudrou* and G.J. Karabatsos

Nuclear Research Center "Democritos", Aghia Paraskevi Attikis, Greece

(Received in UK 22 June 1972; accepted for publication 30 July 1972)

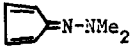
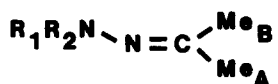
The two methyl groups in p-substituted phenylhydrazones of acetone occupy magnetically non-equivalent sites, thus giving rise in general to two singlet resonance absorptions in the NMR spectrum¹. Y. Shvo and A. Nahlieli² have used the temperature dependence of the methyl region to calculate the barrier to syn-anti isomerization of phenylhydrazones of the dimethyl-ester of oxomalonic acid and of acetone. ΔG^\ddagger values at the coalescence temperature were reported to be very little influenced by the substituent on tricoordinated nitrogen. These results would support a lateral shift rather than a rotational mechanism for the isomerization. It was noted that the separation of the methyl signals is temperature dependent even in the absence of exchange between the two sites, (i.e. when the ratio of exchange is very slow). A Mannschreck and U. Koelle³ have reported that the ring protons in  remain non-equivalent (ABCD pattern) up to at least 150°. We wish to report our observations on a series of compounds of the general structure $R_1 R_2 NN=C(CH_3)_2$. Table I shows the chemical shifts (τ values) of Me_A and Me_B in 1-bromonaphthalene and diphenylether. When R_1 is hydrogen and R_2 a substituted phenyl, the substituent has almost the same influence on the chemical shift of Me_A and Me_B . The dependence of the chemical shift of the methyls on the Hammett σ_p constant is linear. The lower field signal is assigned to the methyl group anti to the R_1 and R_2 groups¹. Column 7 in Table I gives the difference in chemical shifts ($\Delta\tau$) obtained by subtracting the τ -values of Me_A and Me_B of compounds 2-9 from the corresponding τ -values of 1. Changing R_2 from phenyl to methyl (compd 7) has little influence on Me_A but brings Me_B downfield by 0.154 ppm. Changing R_1 from hydrogen to methyl (compd 9), Me_B is shifted downfield by 0.407 ppm whereas Me_A is only slightly influenced. A similar effect is observed for compd 8. The changes of the spectra due to temperature were reversible although partial decomposition was observed for some compounds. Fig 1a shows the spectra of p-nitrophenylhydrazone of acetone at 60°, 180° and back to 60°. The dependence of $\Delta\nu$ (methyl

TABLE I. Chemical shifts of the C-Methyl groups



Compd ^a	R ₁	R ₂	Solvent ^{b,c}	τ		Δτ(R ₂ -C ₆ H ₅)		k cps/deg
				Me _A	Me _B	Me _A	Me _B	
1	H	C ₆ H ₅	A	8.302	8.929			0.076
2	H	p-BrC ₆ H ₄	A	8.401	9.024	0.099	0.095	0.078
			B	8.181	8.585			
3	H	p-ClC ₆ H ₄	A	8.381	8.987	0.079	0.058	0.075
4	H	p-NO ₂ C ₆ H ₄	A	8.495	9.047	0.193	0.118	0.061
5	H	p-CH ₃ C ₆ H ₄	A	8.259	8.860	-0.043	-0.069	0.071
6	H	o-CH ₃ C ₆ H ₄	A	8.300	8.973			0.094
7	H	Me	A	8.250	8.775	-0.052	-0.154	0.060
			B	8.283	8.337	-0.019	-0.592	
8	Me	Me	A	8.283	8.337	-0.019	-0.592	0.024
			B	8.266	8.245			
9	Me	C ₆ H ₅	A	8.244	8.522	-0.058	-0.407	0.027
			B	8.135	8.325			

^aAll hydrazones have been prepared by known methods. Purity was checked by NMR, melting or boiling points. ^bSolvent: A=1-Bromonaphthalene; B=Diphenylether. Solvents A and B were chosen because of the large separation of Me_A and Me_B. In polar solvents the separation is very small (3 cps in hexamethylphosphorotriamide at room temperature). ^cIn 5% solutions at 42°.

separation) on temperature can be expressed as a first order relation, $(\nu_A - \nu_B)_{T_2} = (\nu_A - \nu_B)_{T_1} + k(T_2 - T_1)$ where k depends on the solvent and nature of the N-substituents (Fig 2). The values of k for compounds 1-9 is of the order 10^{-2} cps/degree. The non-equivalence of the methyls is partly due to intermolecular solvent-solute and solute-solute interactions. The rise of temperature reduces these interactions and consequently lowers the $\Delta\nu$ value.

In all cases no coalescence or even broadening of the methyl peaks was observed up to 200° in the solvent used. In the case of compd 8 $\Delta\nu$ at room temperature in 1-bromonaphthalene is 3.25 cps. At 156° the two peaks merge into one. No broadening precedes this merging. This



Fig. 1. a) Compound 4 5% in solvent A. b) Compound 9 5% in solvent A. c) Compound 4 5% in solvent A and in the presence of acetic acid at 170° .

accidental removal of the non-equivalence we believe has nothing to do with a process of exchange. The presence of acid (acetic acid) catalyses the process of syn-anti isomerization as shown in Fig 1c for the p-nitrophenylhydrazone of acetone. As anticipated the presence of acid could reverse the reaction and isomerization could occur as a result of rotation about the C-N bond of the protonated species $\{(Me)_2C-NHNR_1R_2\}^+$ (cf. reference 4).

A number of publications examine the inversion barriers in systems containing C=N bonds such as guanidines, imines etc.) and the results support an inversion (lateral shift mechanism) of the sp^2 hybridized nitrogen atom rather than rotation about the C=N double bond involving a dipolar transition state^{5,6}. The failure to observe any coalescence (exchange) in the systems examined might be due to the mutual repulsion of the lone pairs of electrons on the two nitrogens which destabilize the transition state.

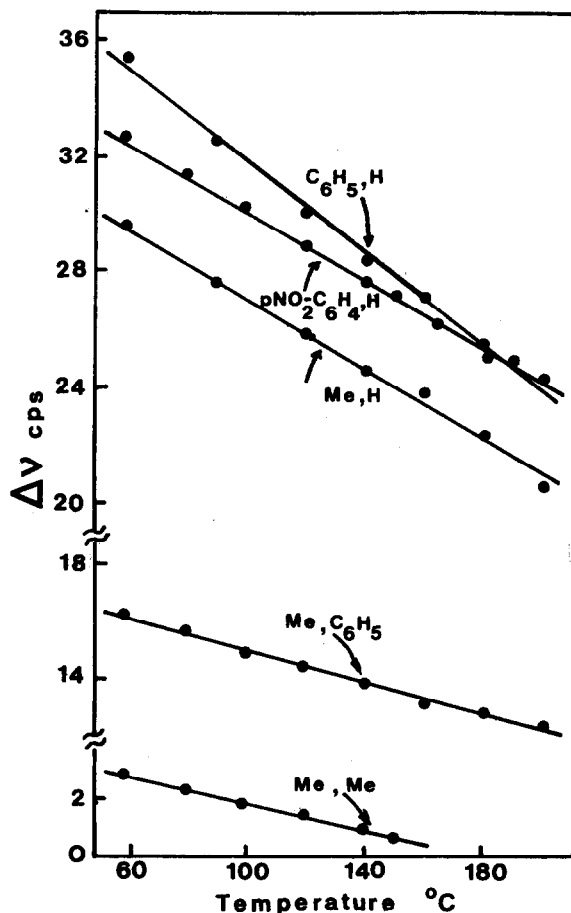


Fig 2. $\Delta\nu$ vs. temperature for compd 1,4,7,8 and 9 in 1-bromonaphthalene.

REFERENCES

*To whom correspondence should be addressed.

1. a) G.J. Karabatsos and R.A. Taller, *J. Am. Chem. Soc.* **85**, 3624 (1963); b) G.J. Karabatsos and K.L. Krumel, *Tetrahedron* **23**, 1907 (1967); c) G.J. Karabatsos and R.A. Taller, *ibid.* **24**, 3557 (1968).
2. Y. Shvo and A. Nahlieli, *Tetrahedron Letters* 4227 (1970).
3. A. Mannschreck and U. Koelle, *Tetrahedron Letters*, 863 (1967).
4. a) A.F. Hegarty and F.L. Scott, *J. Org. Chem.* **33**, 453 (1968); b) J.C. Tobin, A.F. Hegarty and F.L. Scott, *J. Chem. Soc. (B)* 2198 (1971).
5. H. Kessler, *Angew. Chem. Internat. Edit.* **9**, 219 (1970) and refs. therein.
6. I.O. Sutherland, in *Annual Reports on NMR Spectroscopy*. Ed. by E.F. Mooney, Acad. Press. Vol. 4, p. 186-192 (1971) and refs. therein.

Y. Shvo and A. Nahlieli² report a coalescence temperature of 134° for the N-methyl-N-phenylhydrazone of acetone (compd 9) in hexachlorobutadiene ($\Delta G^* = 21$ Kcal/mol). We examined this compound in two different solvents and we observed no coalescence up to 200° under our experimental conditions (Fig 1b). However, when compounds 1,4 and 9 were examined in hexachlorobutadiene or 1,1,2,2-tetrachloroethane (5% solutions) coalescence was observed in the range of 90° to 150°. The exact coalescence temperature depends on the purity of the solvent. Work is in progress to study the behavior of hydrazones in halogen containing solvents.

We thank Mr. S. Chourdakis for assistance.