The Demonstration and Significance of Rotational Barriers in *p*-Dimethylaminophenyldiphenylmethyl Cations

By J. W. RAKSHYS, JUN., S. V. MCKINLEY, and H. H. FREEDMAN*
(*The Dow Chemical Company, Eastern Research Laboratory, Wayland, Massachusetts* 01778)

Summary Rotational barriers exist about the N–aryl bond of *p*′-substituted *p*-dimethylaminophenyldiphenylmethyl cations; these kinetic barriers are substituent dependent and relate directly to π-charge delocalization energies independently determined from thermodynamic data.

THE capacity of the n.m.r. method to produce abundant quantities of rotational barrier data has not always kept pace with a capacity to interpret the significance of these data. Of special interest are those barriers observed in π-delocalized systems whose magnitudes are a potential measure of π-delocalization energy, as suggested by their correlation with theoretically derived measures of π-energies.[1] We now present data which demonstrate that a rotational barrier exists about the N–aryl bond of the *p*-dimethylaminophenyldiphenylmethyl cations (I; X = H, Me, CF_3, or OMe) and that these kinetic barriers relate directly to π-charge delocalization energies independently determined from thermodynamic data.

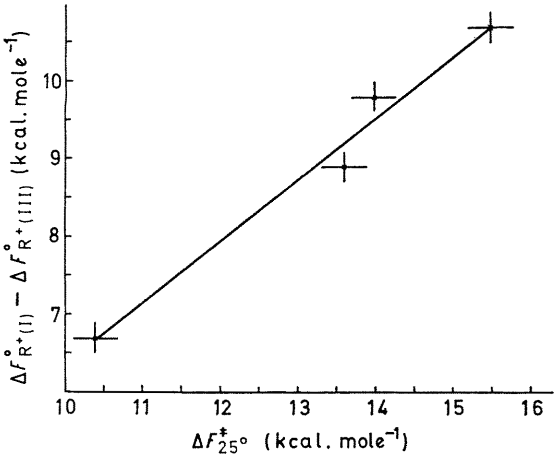
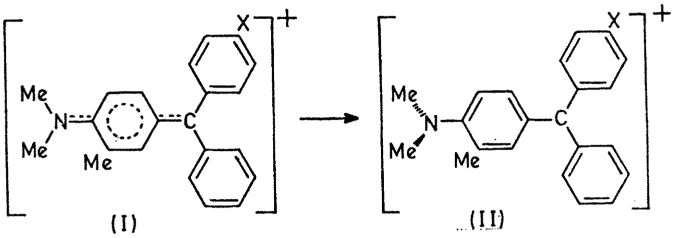


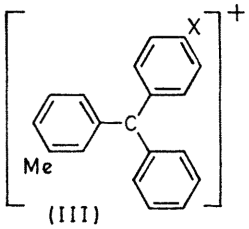
FIGURE. *Plot of π-charge delocalization energies derived from thermodynamic measurements* vs. ΔF‡.

The temperature dependent (but solvent, anion, and concentration independent) spectra of (I) display two non-equivalent N-CH_3 resonances at low temperature ($\Delta\nu_{av.}$ = 8·5 Hz at 60MHz) which broaden and coalesce to a sharp singlet with increasing temperature. This hindered rotation presumably reflects a high N–aryl π-bond order resulting from charge delocalization to nitrogen and clearly defines the ground state of the cations as in (I), with coplanar *p*-dimethylamino-*m*-tolyl, and transition state for rotation, (II), with these groups perpendicular.† Free energies of activation (ΔF‡) at 25° were calculated for the N-CH_3 exchange process by a complete line shape analysis[2] and are listed, along with T_c, in the Table.

Substitution at X strongly affects ΔF‡. The observation that the barrier is increased by electron acceptor groups (*e.g.*, CF_3) and decreased by donor groups (*e.g.*, OMe), unambiguously demonstrates that the π-bond order of the N–aryl bond is sensitive to and dependent on the π-electron density distribution in the cation. These results demonstrate that the effect of substituents on the energy of (II), the postulated transition state, is greater than on (I) and that the effect of multiple substitution on cation energies is not additive. This "saturation" of π-electronic effects on cation stabilization energy has been previously deduced from equilibrium measurements,[3] and our rate-derived results are an independent demonstration of this phenomenon.

It would be of primary significance to establish a quantitative relationship between $\Delta F^{\ddagger}_{(I)\rightarrow(II)}$ (kinetic) and $\Delta F°_{(I)\rightleftharpoons(II)}$ (thermodynamic), since a firm relation has been established between trityl ground state stabilization and π-energies.[4] The triphenylmethyl cation system is uniquely suited to provide this information inasmuch as several experimental techniques are available to assess quantitatively these stabilization energies.[5] We have chosen to use $\Delta F°_{R^+}$ obtained from n.m.r. equilibration data[5c] for this purpose and the Table lists these experimental values for the delocalized cation (I) ($\Delta F°_{R^+(I)}$). For the postulated species (II) a direct $\Delta F°_{R^+}$ measurement is, of course, not possible but it seems legitimate to relate (II), with its unconjugated Me_2N group, to the cations (III), in which the Me_2N is absent,





(III)

by the relationship

$$\Delta F°_{R^+(II)} = \Delta F°_{R^+(III)} + I_{NMe_2}$$

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† We note that a rotational barrier of steric origin does not fit the n.m.r. observations and that the presence of the *m*-CH_3 acts to destabilize the coplanar ground state (I) and thus lower the barrier by an estimated 3 kcal./mol.

‡ A slope of less than unity is clearly incompatible with an electronic argument alone and may suggest, if the experimental difference is significant, that there are small contributions to ΔF‡ other than electronic.

Rate and equilibria data for p-*X-substituted,* p′-*dimethylamino,*m′-*methylphenyldiphenylmethyl cations*

X	T_c(°)	$\Delta F^{\ddagger}_{25°}$(kcal mole)[b]	$\Delta F°_{R^+(I)}$[a]	$\Delta F°_{R^+(III)}$[a]
OMe	−72	10·4	12·0	5·3
Me	−37	13·6	11·3	2·4
H	−13	14·0	10·6	0·8
CF_3	22	15·5	9·0	−1·7

[a] Calculated using n.m.r. method (ref. 5c) relative to triphenylmethyl cation as zero, with estimated error of ± 0·2 kcal./mole.
[b] Error estimated from least squares analysis of Arrhenius plots is ± 0·3 kcal./mole.

where I_{NMe_2} is the destabilizing energy due to the non-conjugated, electronegative NMe_2 group in (II).

The experimental values for $\Delta F°_{R^+(III)}$ are listed in the Table and a plot of the thermodynamic data $[\Delta F°_{R^+(I)} - \Delta F°_{R^+(III)}]$ *vs.* the kinetic data, $\Delta F^{\ddagger}$, is shown in the Figure. The linear relationship, with slope 0·8 ± 0·1 and reasonable intercept −1·5 ± 1 kcal/mol. (equivalent to I_{NMe_2}) demonstrates that the rotational barriers are a direct measure of the π-charge delocalization energy, and the near unity value of the slope confirms our premise that the transition state closely resembles (II)‡.

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[1] *E.g.*: K.-I. Dahlquist and S. Forsen, *J. Phys. Chem.*, 1965, **69**, 4062; J. Sandström, *ibid*, 1967, **71**, 2318; N. P. Marullo, C. B. Mayfield, and E. H. Wagener, *J. Amer. Chem. Soc.*, 1968, **90**, 510; F. A. L. Anet and M. Ahmad, *ibid*, 1964, **86**, 119; V. R. Sandel, S. V. McKinley, and H. H. Freedman, *ibid*, 1968, **90**, 495.

[2] The usual technique (*cf.* A. Allerhand, H. S. Gutowsky, J. Jonas, and R. A. Meinzer, *J. Amer. Chem. Soc.*, 1966, **88**, 3185) of obtaining rate constants at each temperature by matching computer generated spectra with experimental spectra was employed. The basic calculation of C. S. Johnson's program CSJ 3, was adapted for an IBM 1130 computer equipped with accessory plotter. Arrhenius plots were made and $\Delta F^{\ddagger}_{25°}$ was calculated from the usual application of transition state theory.

[3] L. D. McKeever and R. W. Taft, *J. Amer. Chem. Soc.*, 1966, **88**, 4544.

[4] V. Gold, *J. Chem. Soc.*, 1956, 3944; A. Streitwieser, jun., "Molecular Orbital Theory", John Wiley, New York, 1961, pp. 362–6.

[5] (a) N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, jun., *J. Amer. Chem. Soc.*, 1955, **77**, 3044; (b) E. D. Jensen and R. W. Taft, *ibid*, 1964, **86**, 116; (c) A. E. Young, V. R. Sandel, and H. H. Freedman, *ibid*, 1966, **88**, 4532.