Rotational Barriers in 1-Dimethylamino-3-dimethyliminio-2-(*para*-substituted phenyl)propene Perchlorates

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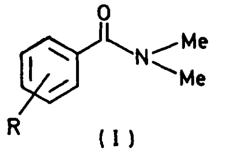
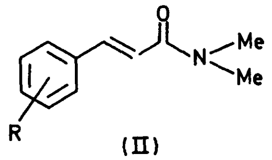
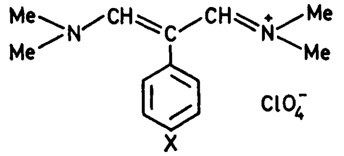
The barriers to internal rotation about the C–N bonds in 1-dimethylamino-3-dimethyliminio-2-(*para*-substituted phenyl)propene perchlorates are not sensitive to the conjugative effects due to change in the *para*-substituent (H, Me, Cl, OMe, NO_2, and CN), consistent with the reported invariance of the u.v. absorption characteristics of these systems for a similar change in the electronic effects on the phenyl group.

THE barriers to internal rotation about the C–N bonds in substituted *NN*-dimethylbenzamides (I) and substituted *NN*-dimethylcinnamamides (II) linearly reflect the change in electron distribution attending a change in the substituent on the phenyl group.[1,2]†


(I)


(II)


(III) a; X = H
b; X = Me
c; X = Cl
d; X = OMe
e; X = NO_2
f; X = CN

At first, it seemed that systems (III), the rotational barriers in which had not apparently been investigated,‡ would show correlations with empirical or calculated parameters reflecting changes in the electron distribution in the molecules similar to those found for the cinnamamides (II) but with, perhaps, a much reduced ρ value § because sensitivity to substituent effects is much smaller in the case of salts compared with the case of the corresponding free bases.[4] However, the results of Kucera and Arnold [5] had indicated that, while changes in the u.v. absorption spectra of 2-substituted aminoiminiopropene salts could be attributed to the steric effects of the 2-substituents, within the series of 2-(*para*-substituted phenyl) compounds (III), for which the steric effect may be presumed to be constant, changing the *para*-substituent does not change the location of the strong absorption at 313—314 nm, though the extinction is somewhat reduced with strongly electron-withdrawing groups (CO_2Et and NO_2). This result could be interpreted as predicting that $\Delta G^{\ddagger}$ for systems (III) would be invariant with change of X. Confirmation of this seemed desirable.

In view of the similarity of structure along the series (IIIa—f) it appeared sufficient to compare the free energies of activation, derived from coalescence temperatures, for these compounds, ignoring entropies of activation.[6] Further, each compound gave spectra which were nearly ideal examples of the equally populated two-site exchange (the uncoupled AB case), having pairs of narrow lines of equal half-widths ($W_{\frac{1}{2}} < 2$ Hz for a separation of *ca.* 85 Hz) for the *N*-methyl groups in the temperature region of slow exchange. Increasing the temperature resulted, in all cases, in equal broadening of the *N*-methyl lines, taken to indicate that there was apparently no differential long-range coupling of the protons of one of the pair of methyl groups on a given nitrogen atom with the vinylic proton on the corresponding α-carbon.¶ These considerations made it seem unnecessary ‖ to use techniques like total line-shape analysis.[9]

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† Rotational barriers in systems (I) show better correlation with σ^+ (correlation coefficient r 0.97) than with σ (r 0.93), a result construed to indicate 'significant conjugation between groups such as *p*-methoxyphenyl and the amide carbonyl group.'[1] The reverse type of correlation (r 0.90 and 0.95 for σ^+ and σ, respectively) found in systems (II) has been interpreted as indicating 'lesser contribution of conjugation in the transmittance of the polar effect.'[2]

‡ A study of the change in the rotational barriers for the unsubstituted systems (a; n = 1—3) has been published.[3] It was

$$\left[\mathrm{Me_2N{=}CH{-}(CH{=}CH)_{\mathit{n}}{-}NMe_2}\right]^+ \mathrm{ClO_4^-}$$

(a)

found that $\Delta G^{\ddagger}$ values decrease with increasing n.

§ The ρ value for the σ parameter for which the best correlation is found.

¶ Systems (IIIa—f) do not seem to resemble *NN*-dimethylformamide [7] in this regard.

‖ The adequacy of approximate methods for calculating $\Delta G^{\ddagger}$ values has been commented upon in many cases.[8]

[1] L. M. Jackman, T. E. Kavanagh, and R. C. Haddon, *Org. Magnetic Resonance*, 1969, **1**, 109.

[2] S. L. Spassov, V. S. Dimitrov, M. Agova, I. Kantschowska, and R. Todorova, *Org. Magnetic Resonance*, 1971, **3**, 551.

[3] G. Scheibe, C. Jutz, N. Seiffert, and D. Grosse, *Angew. Chem. Internat. Edn.*, 1964, **3**, 306.

[4] J. S. Mckennis and P. A. S. Smith, *J. Org. Chem.*, 1972, **37**, 4173.

[5] J. Kucera and Z. Arnold, *Coll. Czech. Chem. Comm.*, 1967, **32**, 1704.

[6] I. O. Sutherland, *Ann. Rep. NMR Spectroscopy*, 1971, **4**, 108.

[7] R. C. Neuman, jun., and V. Jonas, *J. Amer. Chem. Soc.*, 1968, **90**, 1970.

[8] D. Kost, E. H. Carlson, and M. Raban, *Chem. Comm.*, 1971, 656.

[9] L. M. Jackman in 'Dynamic Nuclear Magnetic Resonance,' eds. L. M. Jackman and F. A. Cotton, Academic Press, New York, 1975, pp. 203*ff*.

The $\Delta G^{\ddagger}_{T_c}$ values assembled in Table 1, while being compatible with those reported for systems possessing quaternised nitrogen [formamidinium perchlorate [10] −17.8; compound (a; $n = 1$) [3] −17.0 kcal mol^{-1} at the respective T_c values], show that the rotational barriers in systems (III) cannot be related systematically with the order of variation of conjugative effects as measured by either σ or σ^+ parameters for the substituents.* This result, perhaps, represents a combination of factors, as follows, which tend to diminish the ability of the rotational barriers to reflect changes in electron distribution. (i) The centres of change in systems (III) are far removed from the C–N bonds. (ii) The perturbation of the C–N π-bond order is small because the changes in the electronic effects are dissipated by being distributed between the two substituents on the carbon exocyclic to the phenyl group. (iii) The $\mathrm{C{\cdots}C{\cdots}N^+}$ group is an effective absorber of the changes in electronic effects, more so than the carbonyl group, since the transmitted effects are seen even in cross-conjugated systems like (I) or (II). (iv) Canonical forms in which the C–N π-bond order is altered by a mesomerically active substituent are not likely to be major contributors to resonance in systems (III) because all such forms involve considerable separation of formal charges.†

TABLE 1

Compound [a]	Solvent	T_c/K	$\Delta\nu_\infty$/Hz	$\Delta G^{\ddagger}_{T_c}$/kcal mol^{-1}
(IIId)	$CDCl_3$	360.45	80	17.5
(IIIb)	$CDCl_3$	363.95	83	17.7
(IIIa)	$CDCl_3$	368.05	84	17.8
(IIIc) [b]	$CDCl_3$	361.15	82	17.5
(IIIc) [b]	[$^2H_6$]DMSO	362.05	79	17.6
(IIIf)	[$^2H_6$]DMSO	353.85	81	17.2
(IIIe)	[$^2H_6$]DMSO	354.95	81	17.2

[a] Arranged in accord with the usual trend in substituent effects. [b] Recorded in both solvents in order to check for possible large solvent effect.

EXPERIMENTAL

The dynamic n.m.r. experiments were carried out employing a Varian HA-100D spectrometer operating in the internal lock mode with the tetramethylsilane signal as the internal lock; phase relationships were better maintained when the spectra were field swept. The samples were *ca.* 10% undegassed solutions of the salts (IIIa—f) dissolved in the stated solvents; the plastic stoppers of the sample tubes were tested in each case for their ability to withstand the pressures developed at the higher temperatures (<90°). In all manipulations involving changes of temperature 12—15 min were allowed for re-establishment of thermal equilibrium. Radiofrequency power levels were regulated to avoid saturation.

$\Delta\nu_\infty$ Values given in Table 1 (rounded off to the nearest integral value) are averages of six recordings of the differences between the chemical shifts of the *N*-methyl signals read off the V–4315A system frequency counter while scanning the spectra (in either direction) at 0.4 Hz s^{-1} at different settings (nominally at 3° intervals) of the V-4341/V-6057 variable temperature controller, in the range 20—40°. In no case, within this range, was a systematic variation in the separation of the *N*-methyl signals with temperature observed nor was there detectable line-broadening at the higher temperatures.

Coalescence temperatures were determined as follows, repeating the procedure twice for each case. Several partial spectra were run (covering the *N*-methyl region) near the coalescence point, slightly altering the setting of the variable temperature controller (previously adjusted and calibrated) after each run and checking the radiofrequency phasing, until spectra, visually judged to be acceptable according to the criteria of symmetric flat-topped appearance and approximate parity of the width at half-height with $\Delta\nu_\infty$, were recorded. The corresponding temperatures were then determined from ethylene glycol shifts by applying the van Geet equation.[11]

General Procedure for Preparation of Compounds (IIIa—f).—Compounds (IIIa—f) were prepared by the Vilsmeier–Haack bisformamination of appropriately substituted phenylacetic acids. The latter were prepared following the standard procedure [12] involving the Kindler variation of the Willgerodt reaction of *para*-substituted acetophenones.

TABLE 2

M.p.s of *para*-substituted phenylacetic acids

para-Substituent	M.p. (°C)	Lit.[13] m.p. (°C)
H	77	76
Me	91—93	91—93
Cl	105—106	105—106
OMe	85—86	84—86
NO_2	151—152	150—151
CN	152	151

TABLE 3

M.p.s and analytical data for aminoiminiopropene perchlorates (IIIa—f)

Compound	M.p. (°C)	Lit.[14] m.p. (°C)
(IIIa)	200	201
(IIIb)	162—163	162—163
(IIIc)	147	146—147
(IIId)	132—133	133—134
(IIIe)	225	226
(IIIf)	205 [a]	

[a] Found: C, 51.3; H, 5.45; Cl, 10.8; N, 12.8. $C_{14}H_{18}ClN_3O_4$ requires C, 51.35; H, 5.5; Cl, 10.8; N, 12.8%.

To the stirred reagent prepared by mixing dimethylformamide (11 g), previously cooled to <0°, with phosphoryl chloride (4.6 g) was added a selected phenylacetic acid (0.01 mol). The mixture was gradually brought to 70° (bath temperature) at which temperature it was maintained for 2 h. The bath temperature was then raised to and

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[*] Normally any change associated with a change in *para*-substitution [*e.g.* (IIIa) ⟶ (IIIf)] is expected to reflect the order OMe, Me, H, Cl, CN, NO_2 for a possible linear fit with either σ_p or σ_p^+.[1,2]

[†] Insensitivity of the rotational barriers to the change of *para*-substitution, on the basis of factor (iv), was not anticipated because one tended to look upon electron shifts towards or away from the aminoiminiopropene system as a generalised 'flow,' capable of affecting the C–N π-bond order, rather than as an effect of the build-up of contributing canonical structures.

[10] J. Rauft and S. Dähne, *Helv. Chim. Acta*, 1964, **47**, 1160.

[11] A. L. van Geet, *Analyt. Chem.*, 1968, **40**, 2227; 1970, **42**, 679.

[12] A. I. Vogel, 'A Text-book of Practical Organic Chemistry,' Longman, London, 1968, 3rd edn., pp. 923 *et seq.*

[13] R. C. Weast, 'CRC Handbook of Chemistry and Physics,' The Chemical Rubber Company, Cleveland, 1969—1970, 50th edn., pp. C85—89.

[14] Z. Arnold, *Coll. Czech. Chem. Comm.*, 1961, **26**, 3051; A. Holy, J. Krupicka, and Z. Arnold, *ibid.*, 1965, **30**, 4127.

maintained at 85° until the evolution of gas was complete (*ca.* 4 h). Excess dimethylformamide was removed at reduced pressure. To the cooled residue rendered homogeneous with ethanol (*ca.* 20 ml) was added a cold solution of 70% aqueous perchloric acid (1 equiv.) in ethanol (*ca.* 50 ml). The precipitated aminoiminiopropene perchlorate was recrystallised twice from ethanol.

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