# Rotational Barriers in 2-Aryl-2-norbornyl Cations

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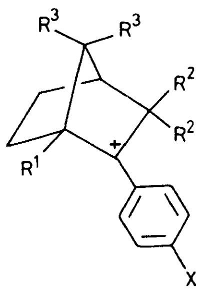
The energy barriers to rotation of the 2-aryl ring in a number of substituted 2-aryl-2-norbornyl cations are reported and give a measure of the extent of π-delocalisation.

The non-linear upward curves of $\Delta\delta C^+$ *vs.* $\sigma C^+$[1] for 2-aryl-2-norbornyl cations where the aryl group contains an electron withdrawing substituent have been widely interpreted to detect the onset of non-classical σ-bridging.[2] This interpretation has been consistently rejected by Brown *et al.*,[3] who have considered several alternative explanations.

For these 2-aryl-2-norbornyl cations the major mode of charge delocalisation is into the aryl ring but no quantitative measure of the extent of π-delocalisation has been reported. The existence of $C^+$–aryl rotational barriers is well established[4] and measurements of the barriers have been made[5] for simple benzylic carbocations under stable ion conditions. The rotational barriers reflect the nature and environment of the cationic centre and for this reason we now report our measurements of the free energy barriers for rotation of aryl rings about the C(2)–Ar bond for cations (**1**)—(**3**) (Table 1).



**a**; X=H
**b**; X=Me
**c**; X=OMe

(**1**) $R^1=R^2=R^3=H$
(**2**) $R^2=H$, $R^1=R^3=Me$
(**3**) $R^3=H$, $R^1=R^2=Me$

**Table 1.** Rotational energy barriers for 2-aryl-2-norbornyl cations (**1**)—(**3**).

| Cation | (**1a**) | (**1b**) | (**1c**) | (**2a**) | (**2b**) | (**2c**) | (**3a**) | (**3b**) | (**3c**) |
|---|---|---|---|---|---|---|---|---|---|
| $\Delta G^{\ddagger}$ (kJ/mol) | 56 | >65 | >68 | <42 | <42 | 48 | <37 | <37 | 39 |
| $T_c$ (°C) | −15 | >30 | >30 | <−90 | <−90 | −40 | <−90 | <−90 | −80 |

The values were calculated[6] from the separation of the *ortho*-carbon signals in the $^{13}C$ n.m.r. spectrum under conditions of slow rotation on the n.m.r. time scale and the coalescence temperature ($T_c$) for the coalescence to a single signal at higher temperatures. The $\Delta G^{\ddagger}$ values are for the coalescence temperature given and although approximate will reflect the relative extent of π-delocalisation.

As expected, electron donating substituents markedly increase the rotational energy barriers within each cation series (**1a**—**c**; **2a**—**c**; **3a**—**c**) due to the greater double bond character of the C(2)–Ar bond associated with increased π-delocalisation *i.e.* ArOMe > ArMe > Ph. In the transition state to rotation there is no overlap between the aryl π-system and the vacant p-orbital at C(2) and for such a rotamer the stabilising–destabilising effect of the aryl moiety is inductive. Substitution of a methyl group on the norbornyl skeleton at C(1) [(**2**)] is seen to decrease significantly the C(2)–Ar rotational barrier by increasing the energy of the rotamer with the aryl ring coplanar with C(1)C(2)C(3), a requirement for efficient π-stabilisation. The introduction of the C(3)-methyls [(**3**)] further decreases the rotational barrier and stability of the coplanar rotamer. The steric constraint to conjugative stabilisation of the C(2) cation for the more hindered systems (**2**) and (**3**) results in a greater demand for alternative stabilisation mechanisms and this is reflected[7] in the less negative $\rho C^+$ values from $\Delta\delta C^+$ *vs.* $\sigma C^+$ plots for these systems compared with the 2-aryl-2-norbornyl cations (**1**).

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