The Study by Nuclear Magnetic Resonance Spectroscopy of the Rotational Isomerism and the Aromatic Character of 6-Dialkylaminofulvenes

By A. P. DOWNING, W. D. OLLIS,* and I. O. SUTHERLAND
(*Department of Chemistry, The University, Sheffield* S3 7HF)

THE kinetics of hindered rotation about the C(6)–N bond[1,2] and the C(1)–C(6) bond[3] of 6-dimethylaminofulvene (I) have been studied using n.m.r. spectroscopy and we now report an extension of these measurements by a study of the effects of 6-aryl and 6-alkyl substituents upon these rotational barriers. These results are of interest in view of the relationship between rotational barriers and aromatic character in these fulvene systems.

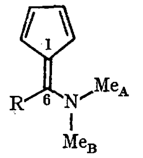
The free energy barriers to C(6)–N rotation are based upon the data previously reported[1] for (I) and the coalescence temperatures[4] of the *N*-methyl signals of (II), (III), and (IV). The free-energy barriers to C(1)–C(6) rotation are based upon the coalescence temperatures of the 2-H and 5-H signals and the 3-H and 4-H signals for (III) and (IV) for which the five-membered-ring proton coupling constants are small in comparison with the signal separations $(\nu_2 - \nu_5)$ and $(\nu_3 - \nu_4)$. The spectra of the ring protons of (I) and (II) were second order so the spectra were simplified by partial deuteriation (~70% random exchange of ring protons) which was achieved by keeping dimethyl sulphoxide solutions of (I) and (II) containing deuterium oxide at 100° for 12 hr. The ring proton signals of partially deuteriated (I) and (II) were observed as broad singlets and coalescence temperatures could readily be measured (Table).

The effects of the 6-substituents upon the rotational barriers in the fulvenes (I—IV) may be steric and electronic in origin. 6-Substituents would be expected to affect the C(6)–N rotational barrier in a similar way to the effects of the same substituents (R) upon the CO–N rotational barrier

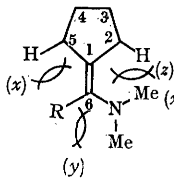
Rotational barriers and temperature dependence of nuclear magnetic resonance spectra of 6-dialkylaminofulvenes (I—IV)

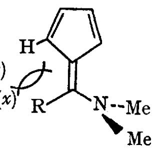
	C(6)–N Rotational barrier				C(1)–C(6) Rotational barrier			
Compound	Solvent	$\nu_A - \nu_B$ (c.sec.$^{-1}$ ± 0·5) (°c)	T_c °c ± 2	$\Delta G^\ddagger$ at T_c[a] (kcal.mole^{-1} ± 0·2)	Solvent	$\nu_A - \nu_B$ (c.sec.$^{-1}$ ± 0·5)	T_c (°c ± 2)	$\Delta G^\ddagger$ at T_c[a] (kcal.mole^{-1} ± 0·5)
(I)	$CDCl_3$–C_6F_6 (1 : 3)	6·5 (−50)	−17	13·5[b]	Me_2SO	13[c]	148	22·1[d]
(II)	$CDCl_3$	12·5 (−73)	−65	10·7	Me_2SO–D_2O	8·25[c]	20	15·5[d]
					Me_2SO	8·50[c]	38	16·4[d]
					$(CD_3)_2CO$	8·75[c]	57	17·5[d]
					$CDCl_3$	8·25[c]	57	17·5[d]
(III)	$CDCl_3$	38·5 (−60)	−34	11·8	Me_2SO	20·0[e]	100	19·2
(IV)	$CDCl_3$	36·5 (−60)	−28	12·1	Me_2SO	19·2[e]	93	18·8

[a] Based upon (ν_A–ν_B) and T_c, using the formula $k = \pi(\nu_A - \nu_B)/\sqrt{2}$ at the coalescence temperature T_c (ref. 4).
[b] Estimated at 0° from the Arrhenius parameters given in ref. 1.
[c] ($\nu_2 - \nu_5$).
[d] Based upon the coalescence behaviour of the partially deuteriated compounds.
[e] ($\nu_3 - \nu_4$).



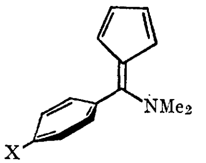
(I) R=H
(II) R=Me
(III) R=Ph
(IV) R=C_6H_4OMe-*p*



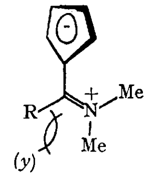


(*x*), (*y*), and (*z*) designate important steric interactions

(V) (VI)



(VII) X=H or OMe



(VIII)

of amides (R–CO–N<).[5] Both aryl and methyl substituents lower the C(6)–N rotational barrier (Table), but the effect of the methyl substituent is greater than the effects of the aryl substituents (*cf.* amides[5]). This behaviour we associate only with the relative steric effects (*x*, *y*, and *z*) of the 6-methyl and 6-aryl substituents in the fulvene ground state (V) and the transition state (VI) for C(6)–N rotation, in which interactions (*y*) and (*z*) are relieved. Interaction (*z*) remains constant throughout the series (I)—(IV), but interaction (*y*) is evidently larger in 6-dimethylamino-6-methylfulvene (II) than in the 6-aryl derivatives (III) and (IV). This is consistent with a ground and transition-state preference for the rotational orientation of the 6-aryl substituents which is shown in (VII). This orientation (VII) inhibits effective conjugation by the aryl substituent in the ground state, accounts for the similarity of the u.v. spectra of the fulvenes (I—IV), and is consistent with the relative chemical shifts of the five-membered-ring proton signals of (I), (III), and (IV). Details of these n.m.r. spectra will be reported in the full paper.

The C(1)–C(6) rotational barriers are also influenced by the 6-substituents (Table). Steric effects are expected to be similar to those for the C(6)–N rotational barriers. Thus, ground-state strain includes the interactions (*x*), (*y*), and (*z*); of these, (*x*) and (*z*) are relieved in the transition state (VIII) for C(1)–C(6) rotation. Since (*x*) is expected to be similar in magnitude to (*y*), from a consideration of the relevant nonbonded interactions (these details will be discussed in the full paper), the steric effects of 6-substituents upon both the C(6)–N and C(1)–C(6) rotational barriers are expected to be similar in magnitude. The relatively small effects of the 6-aryl substituents (Table) suggest that the aryl substituents do not achieve the rotational orientation suitable for conjugation in either the ground state (VII) or the transition state (VIII). The large effect of the 6-methyl group (5·7 kcal. mole^{-1}) may be separated into a steric effect [*ca.* 2·8 kcal. mole^{-1} from the effect of this substituent upon the C(6)–N rotational barrier] and an electronic effect which demonstrates a stabilisation of the carbonium centre of (VIII) by *ca.* 2·9 kcal. mole^{-1}. This is of the same order of magnitude as the stabilisation effect attributed to methyl substituents in certain carbonium-ion reactions.[6] The observed solvent effects upon the C(1)–C(6) rotational barrier of (II) (Table) are consistent with the proposed dipolar character of the transition state (VIII) for C(1)–C(6) rotation.

Consideration of the C(6)–N rotational barrier (13·5 kcal. mole^{-1}) in 6-dimethylaminofulvene (I) shows that the difference in π-electron energy of the ground state (V; R = H) and the transition state (VI; R = H) represents a minimum value (to which steric effects should be added) for the difference in delocalisation energy of the fully conjugated 6-dimethylaminofulvene (I) and the isolated fulvene system (estimated at 12 kcal. mole^{-1})[7] and dimethylamino-group of (VI; R = H). Thus, 6-dimethylaminofulvene has a large delocalisation energy which is greater than 25·5 kcal. mole^{-1}. This result is consistent with the aromatic character of dimethylaminofulvenes previously suggested[8] on the basis of its large dipole moment and chemical behaviour. The measurement of rotational barrier heights thus provides a quantitative approach to the estimation of π-electron delocalisation energies in aromatic systems of the 6-dimethylaminofulvene type.

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