

Conformational inversion in dihydrobenzodioxine radical cations



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The kinetics of the inversion of the dihydrodioxine ring in the radical cations of six dihydrobenzo[1,4]dioxines have been determined by EPR spectroscopy. In the nine compounds for which results are now available, the activation energies E_a range from 22.6 to 47.6 kJ mol⁻¹, and the pre-exponential factors, log A , from 12.8 to 16.2. The barriers appear to be always higher than those in the corresponding hydrocarbon radical cations. Removal of one electron from hexaoxadodecahydrotriphenylene **9** to give the radical cation causes the value of ΔG^\ddagger at 155 K to increase from 30.0 kJ mol⁻¹ in **9** to 36.7 kJ mol⁻¹ in **9**^{•+}. The results are discussed in terms of the various stereoelectronic effects which may be involved.

Dihydro[1,4]dioxines can readily be converted into their radical cations, which can be observed by EPR spectroscopy. The ring inversions occur at a rate which can be measured by monitoring the line shape effects on the signals of the axial and equatorial protons over a range of temperatures, and computer simulation of the spectra gives the rate constants and thence the Arrhenius and Eyring parameters for these reactions.

We have previously applied this technique to the radical cations of 2,3-dihydro[1,4]dioxine **1**^{•+}, 6,7-dimethyl-2,3-dihydro[1,4]dioxine **2**^{•+}, and 2,3-dihydrobenzo[1,4]dioxine **3**^{•+}.¹ The same technique has now been used to determine the kinetics of the inversion of the dioxine ring in the radical cations of 5,8-di-*tert*-butyl-2,3-dihydrobenzo[1,4]dioxine **4**^{•+}, 6,7-dimethyl-2,3-dihydrobenzo[1,4]dioxine **5**^{•+}, 6,7-dimethoxy-2,3-dihydrobenzo[1,4]dioxine **6**^{•+}, 2,3,7,8-tetrahydrobenzo[1,2-*b*;4,5-*b'*]bis[1,4]dioxine **7**^{•+}, 6,7-dihydro-1,3,5,8-tetraoxacyclopenta[*b*]naphthalene **8**^{•+}, and hexahydrobenzotr[is[1,4]dioxine **9**^{•+}. The free energy of inversion in the closed shell parent **9** has also been determined by NMR spectroscopy. We hoped that the results might help to clarify the factors which determine the rates of these ring inversions.

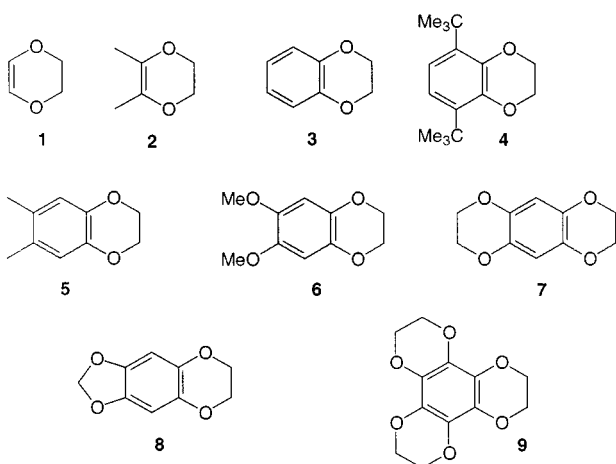
in acetone in the presence of potassium carbonate. Compound **9** was prepared in low yield by the trimerization of 1,4-dioxylene which was formed by the elimination of lithium bromide from 5-bromo-6-lithio-2,3-dihydro[1,4]dioxine.²

The radical cations were generated under a variety of conditions. For kinetic measurements extending to low temperature, the best systems were found to be 1,3-dichloropropane containing aluminium trichloride, or thallium tris(trifluoroacetate) [Tl(TFA)₃] and trifluoroacetic acid (TFAH). Spectra could usually be recorded from *ca.* 360 K down to *ca.* 190 K; at the lower temperatures, different coupling constants were observed for the axial and equatorial methylene protons, and the resulting signals merged at the higher temperatures to give a single time-averaged line. The spectra were computer-simulated and the rate constants for the ring inversion were obtained using the ESRXN program (QCPE no. 209), and thence the Arrhenius parameters. At a given temperature the EPR hyperfine coupling constants were essentially independent of the system which was used to generate the radical cations.

The observed and simulated spectra are illustrated in Fig. 1(a)–6(a), and the corresponding Arrhenius plots in Fig. 1(b)–6(b). Details of the spectra are collected in Table 1, and the Arrhenius parameters are given in Table 2.

In Table 1, the various oxidants and solvent systems which could be used for observing the EPR spectra are shown in column 2. The hyperfine splitting constants and the g values were essentially independent of the nature of the system. The systems which were used for the kinetic study are shown in bold type and the hyperfine coupling constants which are quoted in columns 3, 4, and 5 refer to these conditions, and these values were used for the simulations in Fig. 1(a)–6(a). Within the experimental error, the hyperfine coupling constants of the methylene protons in the fast-exchange mode (generally above *ca.* 340 K) were equal to the arithmetical mean of the values quoted for the corresponding axial and equatorial protons in Table 1. The least satisfactory simulations were those for hexaoxatriphenylene **9** [Fig. 6(b), 281 and 284 K] where the experimental spectra appeared to suffer from a broad, background, sigmoid distortion.

The kinetics of ring inversion in the parent hexaoxatriphenylene **9** were investigated by ¹H NMR spectroscopy. At room temperature the methylene protons appeared as a singlet at δ 4.27. The spectra of **9** in CD₂Cl₂-CF₂ClH solvent over the range 123 to 173 K are shown in Fig. 7. At the lower temper-



Results

The dihydrobenzodioxines **4**–**8** were prepared by treating the corresponding 1,2-dihydroxybenzenes with 1,2-dibromoethane

Table 1 EPR spectra of dihydrodioxines

Dioxine	Oxidant ^a	$a(\text{H}_{\text{ax}})/\text{G}$	$a(\text{H}_{\text{eq}})/\text{G}$	$a(\text{H})/\text{G}$, others	$a(\text{H}_{\text{ax}})/a(\text{H}_{\text{eq}})$	g -value	T/K
1 ^{•+} ^b	g	4.70 (2H)	1.11 (2H)	9.10 (2H)	4.23	2.0040	252
2 ^{•+} ^b	a, c, g	3.55 (2H)	0.85 (2H)	10.80 (6H)	4.18	2.0036	200
3 ^{•+} ^b	b, c + <i>h</i>v	4.01 (2H)	0.95 (2H)	0.4 (2H) 4.57 (2H)	4.22	2.0038	175
4 ^{•+}	f	4.10 (2H)	1.10 (2H)	4.30 (2H)	3.73	2.0037	202
5 ^{•+}	b, c, e	3.30 (2H)	0.70 (2H)	0.70 (2H) 7.00 (6H)	4.71	2.0039	189
6 ^{•+}	f	2.08 (2H)	0.20 (2H)	0.82 (2H) 2.20 (6H)	10.5	2.0038	203
7 ^{•+}	a, b, c, e	2.16 (4H)	0.28 (4H)	0.86 (2H)	7.7	2.0042	223
8 ^{•+}	b, c, d, e	2.20 (2H)	0.28 (2H)	0.94 (2H) 12.08 (2H)	7.8	2.0040	201
9 ^{•+}	b, h	1.13 (6H)	0.17 (6H)	—	6.65	2.0038	^c

^a Oxidants: a, H₂SO₄; b, Ti(TFA)₃-TFAH; c, SO₂-FSO₃H; d, AlCl₃-CH₂Cl₂; e, AlCl₃-Cl(CH₂)₃Cl; f, Ti(TFA)₃-TFAH-Cl(CH₂)₃Cl; g, Hg(TFA)₂-TFAH; h, FSO₃H. ^b See ref. 1. ^c Values of a estimated from simulation of spectra at 229 and 297 K (Fig. 6).

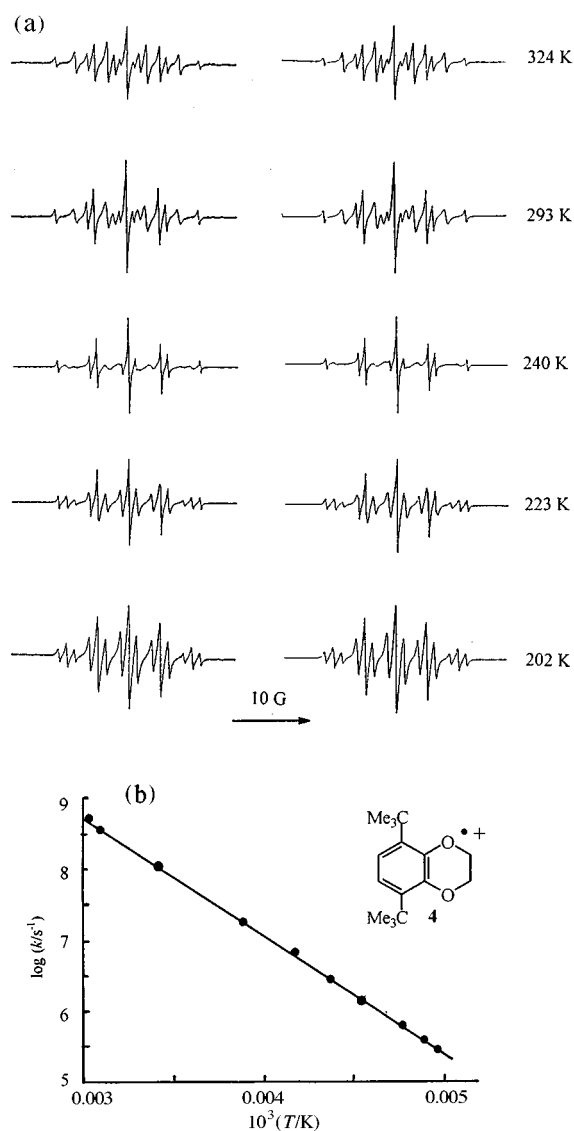


Fig. 1 (a) EPR spectra (left) and their simulations (right) of 5,8-di-*tert*-butyl-2,3-dihydrobenzo[1,4]dioxine **4**^{•+} in Cl(CH₂)₃Cl-Ti(TFA)₃/TFAH. (b) Arrhenius plot for the conformational inversion of **4**^{•+}.

atures the axial and equatorial protons showed separate signals at δ 4.15 and 4.39, which coalesced at 155 K, whence $\Delta G^\ddagger = 30.1 \text{ kJ mol}^{-1}$ and $k(155 \text{ K}) = 2.13 \times 10^2 \text{ s}^{-1}$.

Discussion

When an ether, with formally sp³ hybridised oxygen, is sub-

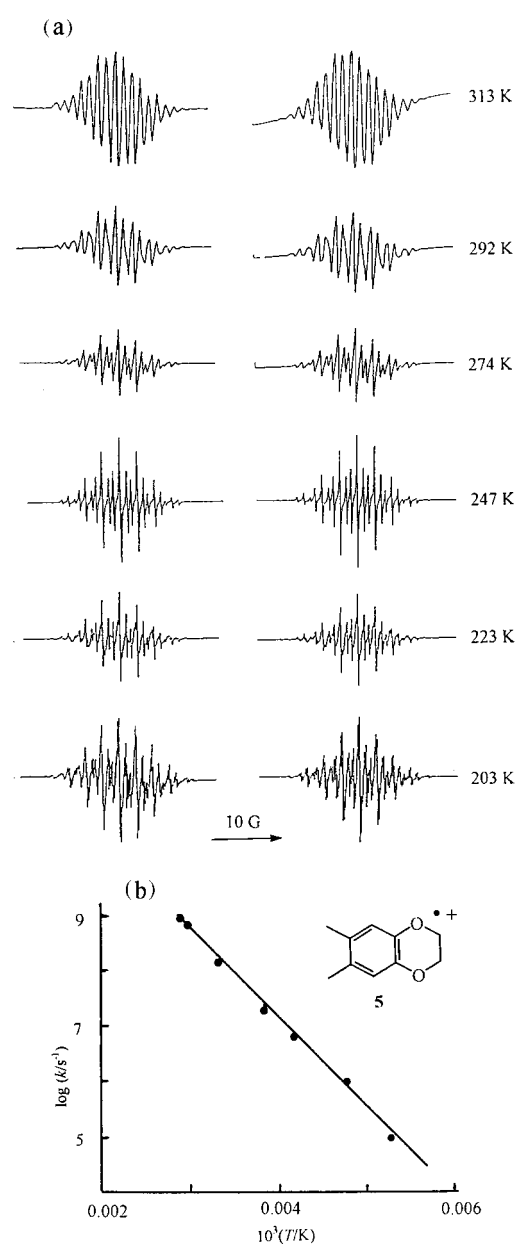


Fig. 2 (a) EPR spectra (left) and their simulations (right) of 6,7-dimethyl-2,3-dihydrobenzo[1,4]dioxine **5**^{•+} in Cl(CH₂)₃Cl-AlCl₃. (b) Arrhenius plot for the conformational inversion of **5**^{•+}.

jected to one-electron oxidation, the hybridisation is changed to sp², and the unpaired electron occupies the 2p orbital.^{3,4} Hyperfine coupling to the hydrogen atoms of the methylene groups in

Table 2 Arrhenius parameters for the ring inversion of dihydrodioxine radical cations

Dihydrodioxine	$E_a/\text{kJ mol}^{-1}$	$\log_{10}(A/\text{s}^{-1})$
1 ^{•+a}	22.6	12.8
2 ^{•+a}	31.4	13.7
3 ^{•+a}	34.7	15.1
4 ^{•+}	31.9	13.7
5 ^{•+}	31.1	13.6
6 ^{•+}	37.0	14.5
7 ^{•+}	46.2	16.2
8 ^{•+}	35.4	14.1
9 ^{•+b}	47.6	16.1

^a See ref. 1. ^b ΔH^\ddagger 45.1 kJ mol⁻¹, ΔS^\ddagger 12.9, ΔG^\ddagger (155 K) 36.7 kJ mol⁻¹.

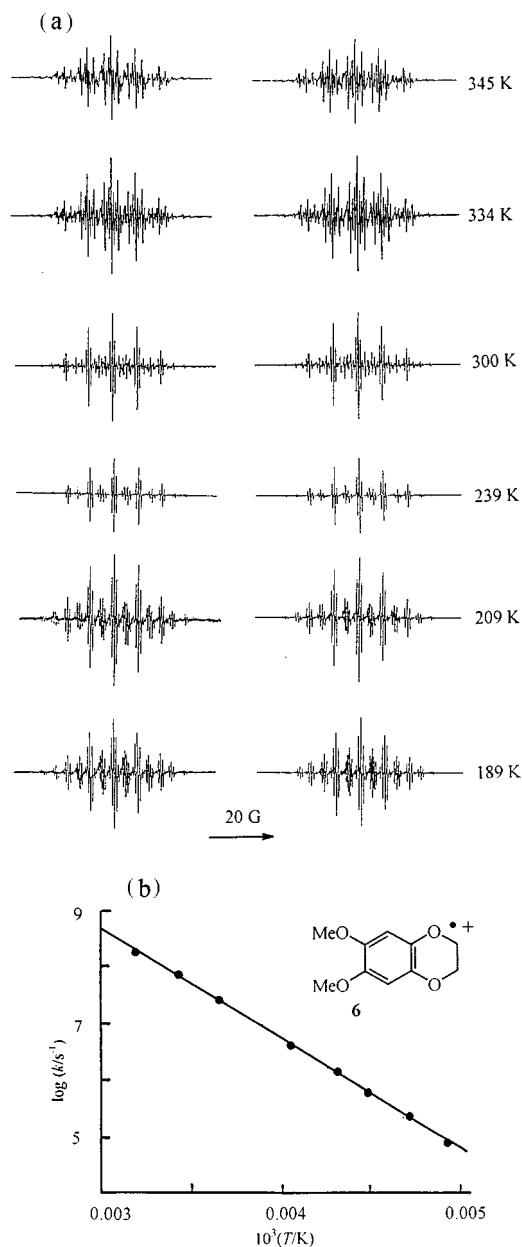


Fig. 3 (a) EPR spectra (left) and their simulations (right) of 6,7-dimethoxy-2,3-dihydrobenzo[1,4]dioxine **6**^{•+} in Cl(CH₂)₃Cl–AlCl₃. (b) Arrhenius plot for the conformational inversion of **6**^{•+}.

the radical cations of compounds **1–9** is thus assumed to arise through hyperconjugation with a singly-occupied p orbital on oxygen as shown in **10**. If the normal $\cos^2\theta$ dependence of $a(\text{H}_\beta)$ holds [eqn. (1)], the variation in the ratio of $a(\text{H}_{\text{ax}})/a(\text{H}_{\text{eq}})$ (Table

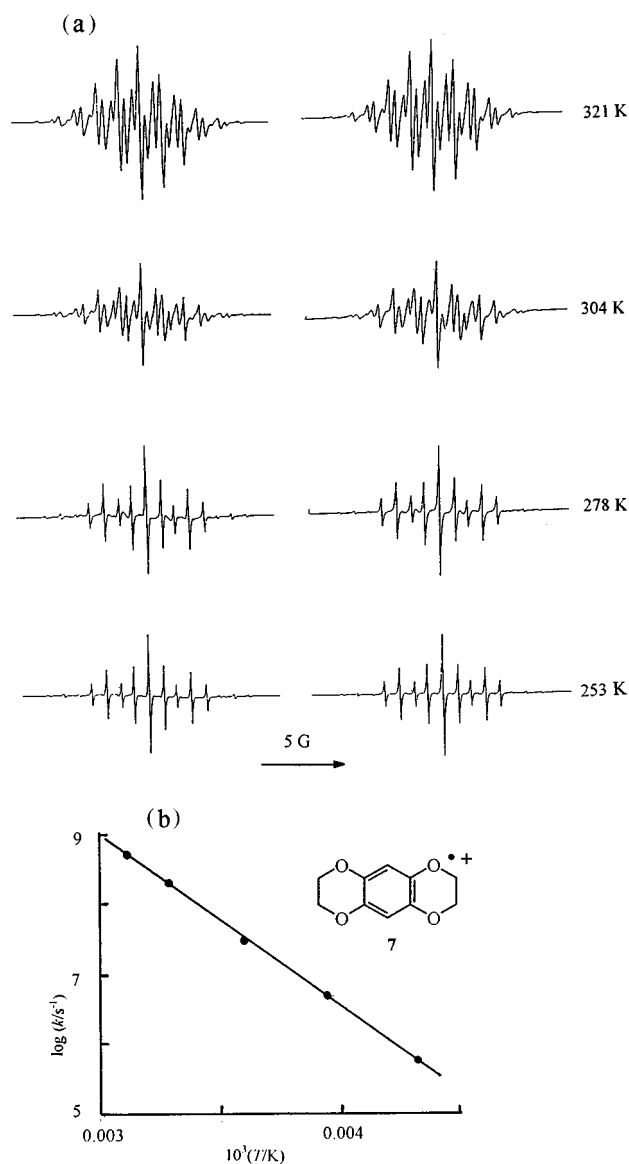
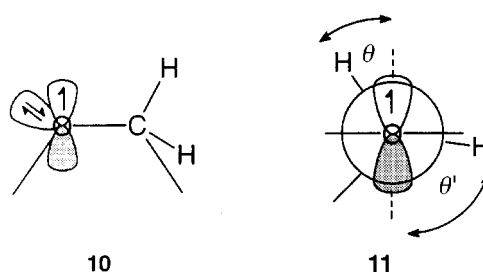


Fig. 4 (a) EPR spectra (left) and their simulations (right) of 2,3,7,8-tetrahydrobenzo[1,2-*b*;4,5-*b'*]bis[1,4]dioxine **7**^{•+} in Cl(CH₂)₃Cl–AlCl₃. (b) Arrhenius plot for the conformational inversion of **7**^{•+}.

$$a(\text{H}_\beta) = \rho_{\text{O}}(A + B\cos^2\theta) \quad (1)$$



1) from 3.73 to 10.5 can be ascribed to variation in the angles θ and θ' (**11**) from about 50 and 70°, respectively, when $a(\text{H}_{\text{ax}})/a(\text{H}_{\text{eq}}) = 3.73$, to 43 and 77° when $a(\text{H}_{\text{ax}})/a(\text{H}_{\text{eq}}) = 10.5$.

The radical cation of dimethyl ether shows $a(\text{H})$ 43 G.³⁻⁵ If the unpaired electron density in the $2p_\pi$ orbital on oxygen, ρ_{O} , is taken to be 0.712 as given by INDO calculation,³ and A in eqn. (1), which will probably be small, is neglected, the constant B is calculated to be *ca.* 120 G. In the symmetrical hexaoxatriphenylene **9**, with $a(\text{H}_{\text{ax}}) = 1.13$ G and $a(\text{H}_{\text{eq}}) = 0.17$ G, θ and θ' are calculated to be 7 and 67° respectively, and eqn. (1) gives ρ_{O} , the unpaired spin density on each of the six oxygen atoms, as

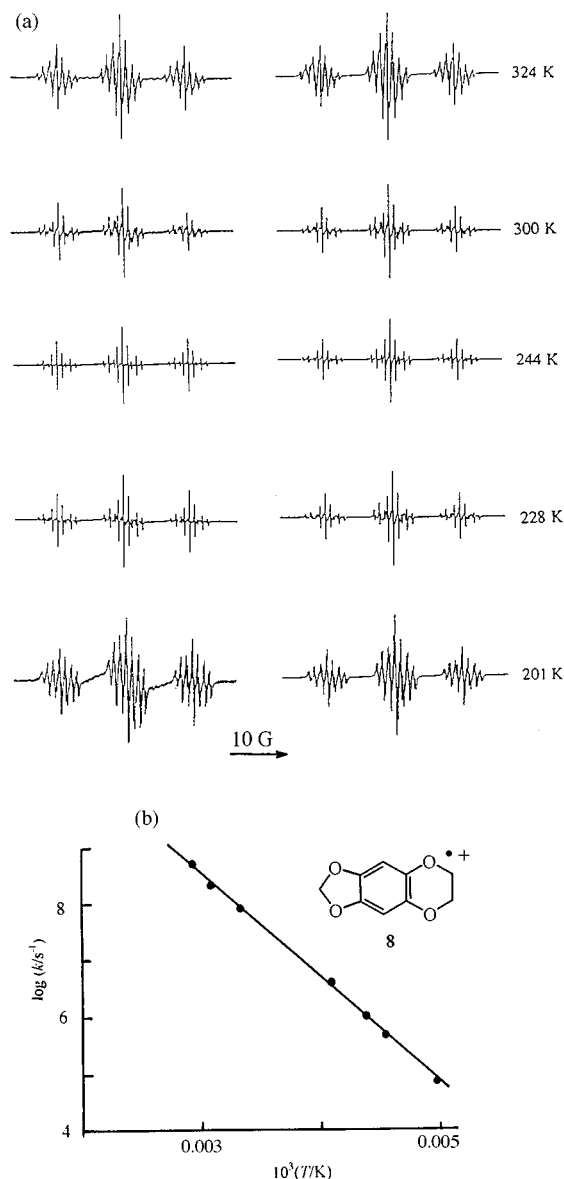


Fig. 5 (a) EPR spectra (left) and their simulations (right) of 6,7-dihydro-1,3,5,8-tetraoxacyclopenta[*b*]naphthalene **8**^{•+}, in Cl(CH₂)₃-Cl-AlCl₃. (b) Arrhenius plot for the conformational inversion of **8**^{•+}.

ca. 0.0095, that is a total of *ca.* 0.057 of the total unpaired spin resides in the 2p_π orbitals on the oxygen atoms, the remainder being associated principally with the π system of the aromatic ring.

The spin density on oxygen is similar in the dihydrodioxines and the corresponding benzodihydrodioxines (compounds **1** and **3**, and **2** and **4**). The large hyperfine coupling of 12.08 G to the methylene group in the dioxolane ring of **8** does not imply a specially high unpaired spin density on the oxygen atoms, but rather is an example of the Whiffen effect where the coefficients of the 2p_π orbitals on the flanking oxygen atoms of the conjugated π system have the same sign.^{4,6}

The EPR spectrum of the radical cation of 5,8-di-*tert*-butyl-2,3-dihydrobenzo[1,4]dioxine, **4**, has been observed before by Malysheva *et al.*⁷ by oxidation with thallium tris(trifluoroacetate) or lead dioxide in trifluoroacetic acid or in a mixture of dichloromethane and trifluoroacetic acid. They report $a(2H, \text{aromatic})$ 4.2 G and, at high temperature, $a(4H)$ 2.65 G, or at low temperature, $a(2H_{ax})$ 4.35 G and $a(2H_{eq})$ 1.1 G. Our corresponding values for oxidation with the Tl(OCOCF₃)₃-CF₃-CO₂H-Cl(CH₂)₃Cl system [Fig. 4(a)] are, at high temperature, $a(2H, \text{aromatic})$ 4.10 G and $a(4H, 2CH_2)$ 2.60 G or, at low temperature, $a(2H, \text{aromatic})$ 4.10 G and $a(2H_{ax})$ 4.10 G and

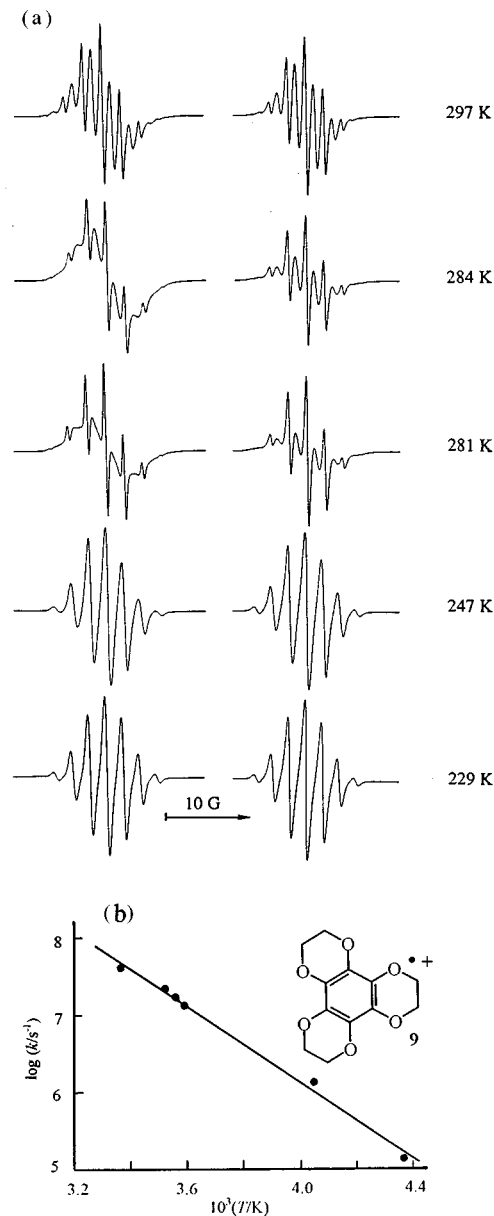


Fig. 6 (a) EPR spectra (left) and their simulations (right) of hexahydrobenzotris[1,4]dioxine **9**^{•+} in FSO₃H. (b) Arrhenius plot for the conformational inversion of **9**^{•+}.

$a(2H_{eq})$ 1.10 G. They followed the changes in the spectrum between *ca.* 330 and 190 K and derived the Arrhenius parameters for the ring inversion, not apparently by simulation, but by measurement at various temperatures of the line separation of pairs of signals which are distinct at low temperature and merge at high temperature. They find that $\log A = 11.96$ and $E_a = 21 \pm 2.1$ kJ mol⁻¹, whereas our values are $\log A = 13.7$ and $E_a = 31.9$ kJ mol⁻¹. The differences between their set of values and ours are hard to understand, and are larger than would be expected to be caused by the different solvent systems. The spectra which are shown in the Russian paper are less well resolved than ours [Fig. 1(b)], but the Arrhenius plot is good.

It is interesting to compare the Arrhenius parameters for the inversion of these dioxine radical cations with those of the corresponding parent spin-paired molecules, and with those of the corresponding hydrocarbons and their radical cations and anions; there appear to be no reports of the EPR spectra of the radical anions of arenes carrying two oxygen substituents, presumably because the electron affinities are too low to allow the usual techniques to be used.

Surprisingly little relevant information is available in the

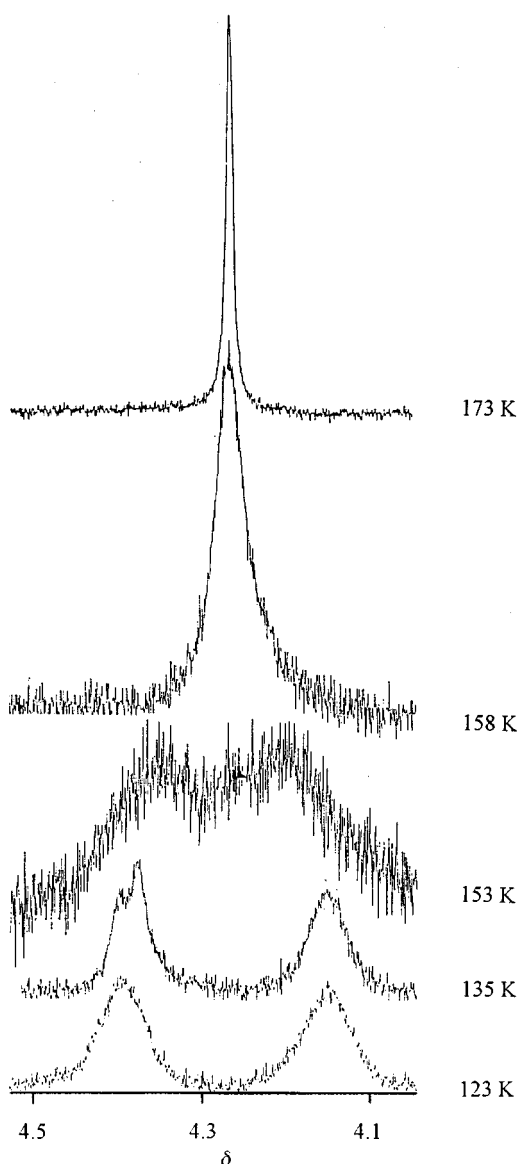


Fig. 7 NMR spectra of hexahydrobenzotris[1,4]dioxine **9** in CD_2Cl_2 - CF_2ClH .

literature.^{8,9} The following factors might be expected to be important.

1. The different bond lengths and angles associated with the oxygen atoms, and the related stretching and bending force constants and torsional and van der Waals interactions.

2. The nature of the wave function in the various species. Differences between the hydrocarbons and their oxygenated analogues will be affected by the conjugation of the 2p orbitals on the oxygen atoms with the π -electron system of the aromatic ring. Further, a molecule M and its radical cation $M^{\cdot+}$ have the same HOMO, but half-occupied in the latter; M and $M^{\cdot-}$ have different HOMOs with different nodal patterns. Insofar as these differences affect the characteristics of the bonds involved in the inversion process, they will lead to differences in the barriers.

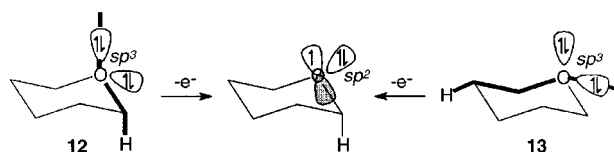
3. Solvation. Radical anions and cations will be solvated more than their spin-paired parents M , which is likely to lead to an increase in the inversion barrier.

4. Counterion interaction. The interaction of a radical anion and its counter cation (usually an alkali metal) is often apparent in the EPR spectrum. Similar interactions must be envisaged between radical cations and their counter anions, though this is not obvious spectroscopically. These interactions again might

be expected to lead to an increase in the inversion barriers of $M^{\cdot+}$ and $M^{\cdot-}$ over that of M .

5. Interaction between the oxygen centres and the $\text{Hg}(\text{TFA})_2$ or $\text{Tl}(\text{TFA})_3$ oxidants, or their reduced forms, behaving as Lewis acids.

6. Any anomeric¹⁰ or homoanomeric¹¹ effects. In saturated oxygenated radical cations, the anomeric (**12**) and homoanomeric (**13**) effects would be expected to be larger in M , with formally sp^3 hybridised oxygen, than in $M^{\cdot+}$ with formally sp^2 hybridised oxygen, with again an effect on the ring inversion barrier.



In the dihydrobenzodioxines studied here, however, the oxygen can be regarded as being already formally sp^2 hybridised in M to allow conjugation of the 2p electron pair with the aromatic ring, and any decrease in the anomeric and homoanomeric interactions in going to $M^{\cdot+}$ would be expected to be smaller.

The results in Table 2 can be discussed against this background.

The effect of oxygenation of the ring

Oxygenation of saturated rings usually reduces the inversion barrier,¹² but the free energy of conformational inversion of cyclohexene, 3-oxacyclohexene, and 3,6-dioxacyclohexene **1** is 22.2 (at 113 K),^{13,14} 27.6 (at 133 K),¹² and 30.5 (at 148 K) kJ mol^{-1} ¹⁵ respectively, oxygenation *increasing* the barrier. Factor 1 above therefore does not appear to be dominant, and the effect of oxygen has been ascribed to stabilisation of the ground state of the oxacyclohexenes by electron delocalisation involving the electrons in the 2p $_{\pi}$ orbitals on oxygen and the olefinic π -bond (factor 2 above).¹²

Our results for the radical cations octahydroanthracene $^{\cdot+}$ (E_a ca. 17 kJ mol^{-1})¹⁶ and tetraoxaanthracene $^{\cdot+}$ **7** $^{\cdot+}$ (46.2 kJ mol^{-1}), and for dodecahydrotriphenylene $^{\cdot+}$ (20.1 kJ mol^{-1})¹⁶ and hexaoxadodecahydrotriphenylene $^{\cdot+}$ **9** $^{\cdot+}$ (46.7 kJ mol^{-1}) are consistent with this. Bushweller and O'Neil's model¹² can satisfactorily explain this, the overlap now being with the π system of the aromatic ring. Any repulsion between non-bonded sp^3 hybridised methylene groups in adjacent rings in the transition state for the inversion of dodecahydrotriphenylene $^{\cdot+}$ ¹⁶ would be replaced in **9** $^{\cdot+}$ by the analogous repulsion of non-bonding electrons on sp^2 hybridised oxygen (factor 3),¹⁷ but our results do not serve to distinguish this possibility from the other factors which may be operating.

In a preliminary note,¹⁸ Furukawa *et al.* have reported that the activation energy for the ring inversion in the tetrathiaoctahydroanthracene radical cation (the tetrathia equivalent of **7** $^{\cdot+}$) is 11.3 kJ mol^{-1} (and that of the corresponding octahydrophenanthrene derivative is 14.2 kJ mol^{-1}). This reduction in the barrier on going down the chalcogen group of the Periodic Table is in line with previous observations, and has been ascribed to a reduction of the torsional barrier, the bending strain being unimportant.¹⁹ Details of Furukawa's work, however, do not appear to have been published.

Substituent effects

It is difficult to do more than note the effects of substituents on the inversion barriers.

Dialkylation of the aromatic ring in **3** $^{\cdot+}$ (E_a 34.7 kJ mol^{-1}) to give **4** $^{\cdot+}$ (E_a 31.9 kJ mol^{-1}) or **5** $^{\cdot+}$ (E_a 31.1 kJ mol^{-1}) reduces the inversion barrier.

Table 3 Barriers to ring inversion in related spin-paired molecules and their radical cations and anions

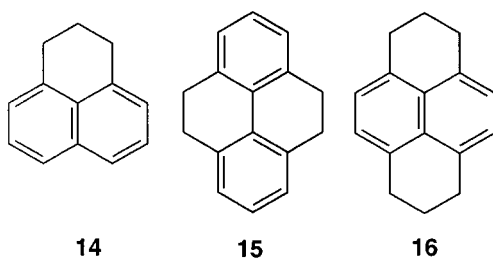
	1 ^a	9 ^b	14 ^c	15 ^a	16 ^a
M ^{•+}	22.6 ¹	36.74		20.5 ²¹	32.2 ²²
M	31.9 ¹⁵	30.12	34.89 ²³	<33.5 ²⁴	
M ^{•-}			30.3 ²⁵	36.4 ^{21,26,27}	30.0 ²⁸

^a Values of E_a in kJ mol^{-1} . ^b Values of ΔG^\ddagger (155 K) in kJ mol^{-1} . ^c Values of ΔG^\ddagger (173 K) in kJ mol^{-1} .

The highest values of E_a occur with $7^{•+}$ (42.0 kJ mol^{-1}) and $9^{•+}$ (47.3 kJ mol^{-1}) which contain three and four fused six-membered rings respectively, and this might be seen to result from the extra stiffening of the molecule as a result of the fusion. However the replacement of one of the six-membered dioxine rings in $7^{•+}$ by a 5-membered dioxolane ring to give $8^{•+}$ reduces the barrier to 35.4 kJ mol^{-1} and replacing this dioxolane ring by two methoxy groups to give $6^{•+}$ brings about a small increase to 37.0 kJ mol^{-1} .

The effect of orbital occupancy

Very little information is available on the effect on the inversion barrier of adding or removing an electron from the spin-paired parent molecule.²⁰ The information which is available in the literature and from the present work is summarised in Table 3.



We suggested that the inversion barrier in the dioxine radical cation $1^{•+}$ was smaller than that in **1** because removal of an electron reduced the net π bond order in the region of the molecule about which rotation occurred.¹ Iwaizumi *et al.* considered two factors which might account for the barrier in the hexahydrodipyrrene radical anion $16^{•-}$ being less than that in the radical cation $16^{•+}$. First, in the radical cations, the positive charge caused a contraction of the electron distribution, resulting in smaller overlap integrals and a decrease in the bending and stretching force constants. Second, hyperconjugative stabilisation by the methylene groups, which was expected to be more important in the transition state than in the reactants, should be larger in the radical cations than in the anions.²⁶

In hexaoxadodecahydrotriphenylene, however, ΔG^\ddagger for **9** and $9^{•+}$ (with FSO_3^- counterion in FSO_3H) is 30.2 and 36.9 kJ mol^{-1} respectively, the barrier increasing with oxidation. It is difficult to rationalise this change in the order of the barriers between the systems **1** and **9**. It is larger than one would expect to arise from the differences in the counterion and the solvent (factors 4 and 5), and the nodal pattern of the SOMOs of both systems (factor 2) is similar (though that of $9^{•+}$ is doubly degenerate).

Conclusion

We have observed no significant dependence of the EPR hyperfine coupling constants on the various systems which have been used for generating the radical cations, which might be taken to suggest that the interactions listed in factors 3, 4, and 5 above are not important in determining the inversion barriers. Any anomeric or homoanomeric effects in the dihydrobenzodioxines are difficult to assess, but are likely to be small. The domin-

ant factors in determining the barriers to ring inversion in the spin-paired and odd-electron molecules considered here are probably 1 and 2 as listed above, but many more data on related families of compounds will be needed before any convincing interpretation can be drawn.

Experimental

EPR spectra were recorded on a Bruker ESP300 spectrometer which was fitted with a 500 W high pressure mercury arc focussed on the cavity, and provided with neutral (metal gauze) and glass (Pyrex and soda glass) filters. Infrared radiation was removed by passing the light beam through a water-cooled solution of CoSO_4 and NiSO_4 . Computer simulations of experimental spectra were carried out using the Bruker EPR-Simulation Program Version 1.0, or, for the kinetic spectra, the ESRXN program (QCPE no. 209).

The radical cations were generated as follows (see Table 1). *Methods a, c, and h.* A solution of the substrate (0.05 mg) in H_2SO_4 or FSO_3H (1 cm^3) at room temperature, or $\text{SO}_2\text{-FSO}_3\text{H}$ (*ca.* 1:1, v/v) at 230 K, was deaerated with a stream of nitrogen for 5 min. *Methods b and g.* A mixture of either $\text{Hg}(\text{TFA})_2$ or $\text{Tl}(\text{TFA})_3$ (5 mg) in TFAH (1 cm^3) at 260 K was deaerated with nitrogen. The substrate (0.05 mg) was added and the mixture was deaerated for a further 2 min. *Methods d and e.* A solution of the substrate (0.05 mg) and AlCl_3 (*ca.* 10 mg) in CH_2Cl_2 or $\text{Cl}(\text{CH}_2)_3\text{Cl}$ (1 cm^3) at 240 K was purged with nitrogen for 5 min. *Method f.* A solution of $\text{Tl}(\text{TFA})_3$ in $\text{Cl}(\text{CH}_2)_3\text{Cl}$ (1 cm^3) containing one drop of TFAH was deaerated with nitrogen; the substrate (0.05 mg) was added, and the solution was purged for a further 5 min.

Compounds **4-9** were prepared by literature methods, and showed the following characteristics. Chemical shifts are given in ppm.

5,8-Di-tert-butyl-2,3-dihydrobenzo[1,4]dioxine 4²⁹ mp $44\text{--}45^\circ\text{C}$ (lit.,²⁹ $48\text{--}49^\circ\text{C}$). Found C, 77.24; H, 9.84. $\text{C}_{16}\text{H}_{24}\text{O}_2$ requires C, 77.38; H, 9.74%. δ_{H} (200 MHz; CDCl_3) 1.34 (18H, s, Me_3C), 5.90 (2H, s, OCH_2O), 6.71 (2H, s, ArH).

6,7-Dimethyl-2,3-dihydrobenzo[1,4]dioxine 5³⁰ mp $71\text{--}74^\circ\text{C}$ (lit. $72\text{--}74^\circ\text{C}$ ³⁰). δ_{H} (200 MHz; CDCl_3) 2.14 (6H, s, CH_3), 4.21 (4H, s, $\text{OCH}_2\text{CH}_2\text{O}$), 6.64 (2H, s, ArH).

6,7-Dimethoxy-2,3-dihydrobenzo[1,4]dioxine 6³¹ mp $91\text{--}92^\circ\text{C}$ (lit. $90\text{--}90.5^\circ\text{C}$ ³¹). Found C 61.10; H, 6.35. $\text{C}_{10}\text{H}_{12}\text{O}_4$ requires C, 61.22; H, 6.16%. δ_{H} (200 MHz; CDCl_3) 3.79 (6H, s, OCH_3), 4.20 (4H, s, $\text{OCH}_2\text{CH}_2\text{O}$), 6.45 (2H, s, ArH).

2,3,7,8-Tetrahydrobenzo[1,2-b;4,5-b']bis[1,4]dioxine 7. The 400 MHz ^1H NMR spectrum exhibited a single peak at δ 4.22 at 293 K, which showed no sign of broadening down to 130 K. The EPR spectrum was observable, without photolysis, in concentrated H_2SO_4 , $\text{CF}_3\text{CO}_2\text{H-Tl}(\text{OCOCF}_3)_3$, $\text{SO}_2\text{-FSO}_3\text{H}$, or $\text{Cl}(\text{CH}_2)_3\text{Cl-AlCl}_3$, and, at 321 K, consisted of a simple binomial nonet of 1:2:1 triplets. In $\text{Cl}(\text{CH}_2)_3\text{Cl-AlCl}_3$, the spectrum could be studied between 174–321 K.

6,7-Dihydro-1,3,5,8-tetraoxacyclopenta[b]naphthalene 8³² mp $88\text{--}89^\circ\text{C}$ (lit.,³² 89°C). δ_{H} (200 MHz; CDCl_3) 4.17 (4H, s, $\text{OCH}_2\text{CH}_2\text{O}$), 5.83 (2H, s, OCH_2O), 6.41 (2H, s, ArH).

Hexahydrobenzotris[1,4]dioxine 9² δ_{H} (400 MHz; CDCl_3) 4.27 (lit.,² 4.30).

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