The Effect of Atropisomerism upon Electrophilic Aromatic Reactivity: Detritiation of Hexa- and Tetra-*o*-phenylene

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Summary The first measurements of the electrophilic reactivity of aromatic atropisomers (crown and helical hexa-*o*-phenylene) and also of (crown) tetra-*o*-phenylene have been made *via* protiodetritiation; the reactivity order is: helical-HP > crown-HP > crown-TP, which parallels the extent of coplanarity of adjacent phenyl rings.

Hexa-*o*-phenylene exists in two stable conformers (**1**) and (**2**), known as the crown, and helical (or screw) isomers, respectively;[1] these cannot interconvert without bond breaking and are therefore atropisomers. It is of interest to know the effect of this atropisomerism upon aromatic reactivity, there being no previous information. The absence of steric hindrance in acid-catalysed hydrogen exchange and abundance of kinetic data for related molecules in this reaction (specifically, protiodetritiation) made it the reaction of choice. The exchanging medium was trifluoroacetic acid (TFA), and tritium was incorporated into the molecules *via* exchange with TFA–T_2O and then removed under kinetic conditions using TFA alone. For comparative purposes tetra-*o*-phenylene [which exists only in the crown form (**3**)] was also examined. For all of the compounds, mixed kinetic-order plots were obtained as expected,† and these were resolved into their first-order

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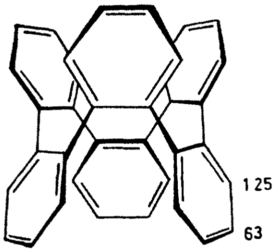
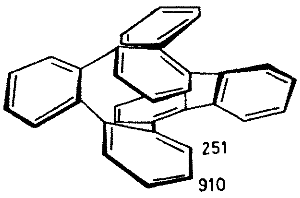
† Difficulty was encountered in this work owing to the extreme insolubility of these aromatics, and to the fact that they form inclusion compounds with most common solvents. Thus exchange could not be measured in a TFA–cosolvent mixture, and the insolubility problem precluded determination of the position of exchange by n.m.r. methods. To reduce the insolubility problem, kinetic studies were carried out at 125 °C, and the derived partial rate factors were converted to those for 70 °C, the standard condition for detritiation, by means of the Arrhenius equation.



(1)



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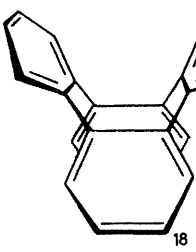


(3)

components [leading to the partial rate factors and σ^+-values (Table)].

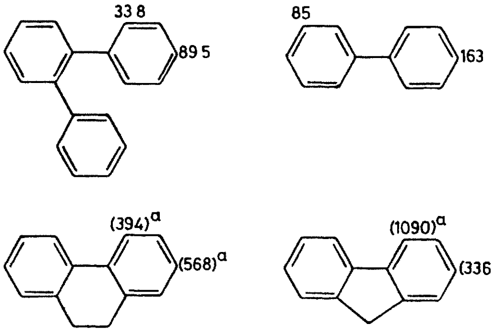
TABLE. Rate coefficients and partial rate factors for detritiation

Compound	Position	10^7k/s^{-1}	f (125 °C)[a]	f (70 °C)	σ^+
(**1**)	4	264	35.3	63	−0.205
(**1**)	3	9	1.2	1.25	
(**2**)	4	2650	355	910	−0.34
(**2**)	3	875	117	251	
(**2**)	[b]	*ca.* 95	13	20	
(**3**)	4	90	12	18	−0.14
(**3**)	3	20	2.7	3	

[a] For benzene under these conditions, $k = 7.47 \times 10^{-7}$ s^{-1} (ref. 2). [b] See the text.

The partial rate factors are assigned in (**1**)—(**3**) assuming that the 4-position will be the most reactive. However, it would be expected that the 3-position (*ca.* *m*-Ph × *o*-Ph) and the 4-position (*ca.* *m*-Ph × *p*-Ph) would have fairly similar reactivities (since $f_o^{\mathrm{Ph}} = 85$, $f_p^{\mathrm{Ph}} = 163$)[3], so doubt attaches to the very low partial rate factors assigned to the 3-positions of tetra-*o*-phenylene and crown hexa-*o*-phenylene. Since it is inconceivable that this is a steric effect, and we have no other reasonable interpretation, we are inclined to the view that these low values refer to an impurity (or decomposition product), in which case the values assigned to the 4-positions are in fact the *average* values for the 3- and 4-positions. However, this problem does not affect the main features of the results which are as follows.

(i) In helical hexa-*o*-phenylene the benzene rings can slide past each other making them equivalent. If this process is fast relative to the exchange then there are only two distinguishable hydrogens, but if slow, there are six (which have been identified by n.m.r. spectroscopy).[4] We observed two principal exchange rates (and a third slow rate which corresponded to only 12% of the overall exchange and could again be due to a decomposition product). Our assignment of the partial rate factors gives the log f_o: log f_p value of 0.86 in excellent agreement with that (0.865) which applies to a wide range of substituents.[5] These factors may be compared with those (Scheme) for related molecules[3,6] which have variable angles between the phenyl rings. (The values given for fluorene and 9,10-dihydrophenanthrene are the observed values divided by 5 to allow approximately for the effect of the alkyl groups.) In hexa-*o*-phenylene each 4-position is *meta* to a phenyl ring (which produces a deactivation of 0.7)[3] and *para* to another which itself contains an *o*-phenyl-substituent. The remote effect of this latter‡ will produce an activation of antilog [(−log 85/4)] = 3-fold so the combined effect of these substituents should be a *ca.* 2-fold activation. The same applies to the 3-position so that the 'corrected' partial rate factors are 125 and 455, *i.e.* slightly less than the corrected values for dihydrophenanthrene which are in excellent agreement with prediction based on models which show the angle between the rings to be slightly less than in dihydrophenanthrene.



SCHEME. [a]See the text.

The presence of four phenyl rings held *trans* coplanar to one another (as in *p*-cyclophane) would predict enhanced exchange rates. Since these were not observed, rapid interconversion of the rings relative to the rate of exchange is further indicated.

(ii) The rings in crown hexa-*o* phenylene are nearly orthogonal as they are in *o*-terphenyl, and the partial rate factors for the 4-positions are comparable, the hexa-*o*-phenylene value being the smaller as it should be owing to the effect of the additional *m*-phenyl substituent.

(iii) Models indicate tetra-*o*-phenylene to be less flexible than crown hexa-*o*-phenylene. Consequently, adjacent phenyl rings in TP are less able to move towards coplanarity to facilitate conjugative stabilisation of the transition state for substitution. The partial rate factor for

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‡ The ρ-factor for substituent effects in electrophilic substitution of biphenyl is 4-fold less than in benzene (R. Taylor, unpublished work).

exchange at the 4-position is therefore less than at the 4-position of crown hexa-*o*-phenylene.

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