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A THEORETICAL AND EXPERIMENTAL INVESTIGATION OF ACID CATALYZED REARRANGEMENTS OF SMALL [*n*]CYCLOPHANES

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ABSTRACT

The difference in reactivity of small [*n*]cyclophanes towards CF_3CO_2H is discussed in terms of charge densities, strain energies and proton affinities. These data are calculated with MNDO and MINDO/3 for *para*-, *meta*- and *ortho*-cyclophanes and for their *ipso*-protonation products; an attempt is made to transform gas phase ΔH^0_f values into liquid phase ΔH^0_f values. Experimental evidence is presented that the acid catalyzed rearrangement of [5]paracyclophane to its *ortho*-isomer proceeds via two consecutive 1,2-carbon shifts without deprotonation; intermediate adducts were identified by NMR-spectroscopy. Thus, a gradual shift in reaction pattern in the series [4]-, [5]- and [6]paracyclophane is observed experimentally, in line with the calculational results.

INTRODUCTION

Small [*n*]cyclophanes continue to receive a considerable amount of interest. This class of compounds gives insight into the behavior of aromaticity in heavily distorted bridged aromatic systems.[1] [6]Paracyclophane turned out to be reasonably stable at room temperature,[2] but the next lower homologue [5]paracyclophane decomposes above 0 °C;[3a] only a limited increase of stabilization could be achieved by electron-withdrawing groups at the aromatic ring.[3b–d] The thermal stability further decreases on going to [4]paracyclophane which decomposes already at −60 °C.[4] The [*n*]metacyclophane series shows a similar trend. [6]Metacyclophane[5a] and [5]metacyclophane[5b] are stable at room temperature whereas [4]metacyclophane could be established only indirectly as an intermediate in a characteristic dimerization reaction.[6] This dramatically increased reactivity compared to ordinary (flat) benzene derivatives is evidently caused by strain and increases as the bridge becomes shorter. The strain energies in [*n*]paracyclophanes have been calculated to be 88·4, 62·9 and 44·4 kcal mol^{-1} for $n = 4$ to 6, respectively, [7a] while in the [*n*]metacyclophane series the strain energies are 71·9, 46·1 and 31·9 kcal mol^{-1} for $n = 4$ to 6, respectively;[7] throughout this paper 1 kcal = 4·184 kJ.

One of the characteristic reactions of small cyclophanes is protonation. The resulting benzenonium ions can rearrange to less strained isomers by 1,2-carbon shifts or can be trapped by nucleophiles. A general reaction scheme is outlined in Scheme 1.

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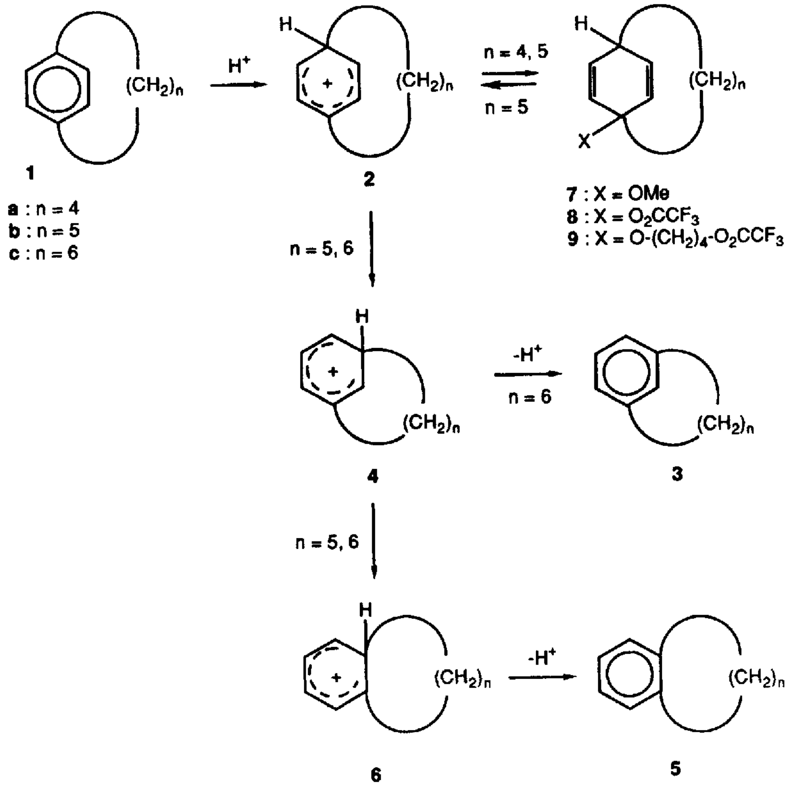
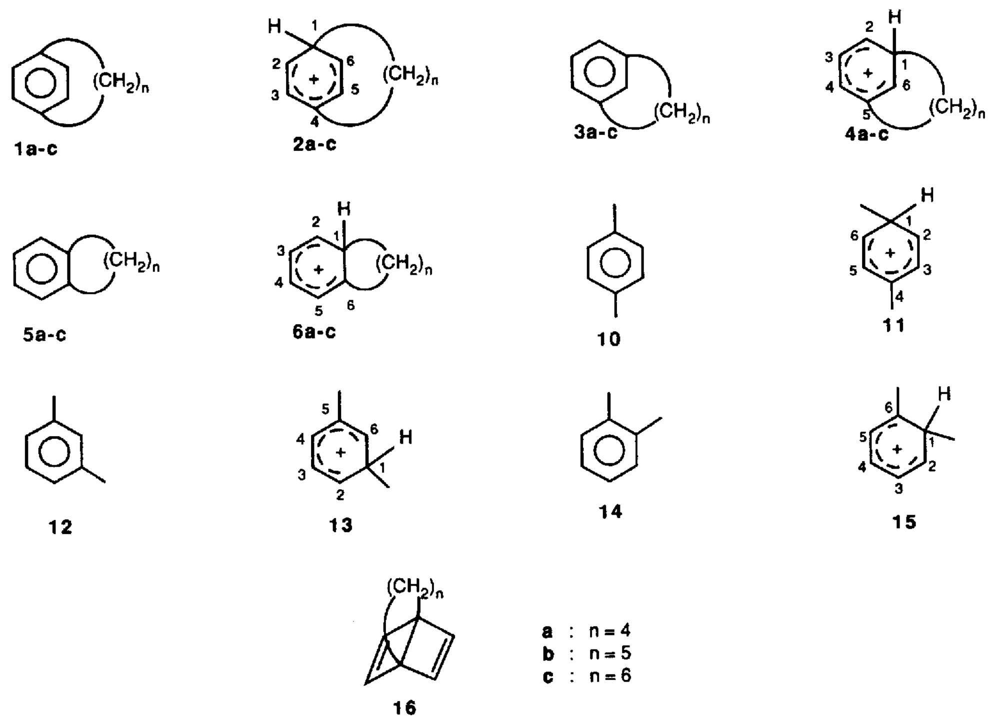


Scheme 1

On treatment with trifluoroacetic acid, [6]paracyclophane (**1c**) has been reported to give [6]metacyclophane (**3c**) and 5,6,7,8,9,10-hexahydrobenzocyclooctene (**5c**) in a ratio of 1:3, while **3c** did not rearrange under these conditions to its *ortho*-isomer **5c**; this implies that **5c** was formed via two consecutive 1,2-C-shifts without deprotonation and reprotonation.[8a] Treatment of **1c** with CF_3CO_2H in MeOH did not yield addition products such as **7c**–**8c**.[8b] In sharp contrast, [4]paracyclophane (**1a**), photochemically generated from its 1,4-tetramethylene Dewar benzene precursor in the presence of trifluoroacetic acid, did not furnish, as expected, tetralin (**5a**), but **8a** and **9a**; [4a] apparently, instead of being rearranged by acid catalysis to its *ortho*-isomer **5a**, **1a** underwent addition reactions. Photochemical generation of **1a** in acidic methanol solution yielded **7a** as the major product.[4] [5]Paracyclophane (**1b**) shows an intermediate behavior, as will be shown later in this paper. In the *meta*-series, [5]metacyclophane (**3b**) gave 6,7,8,9-tetrahydro-5*H*-benzocycloheptene (**5b**) upon treatment with CF_3CO_2H in chloroform,[9] and [4]metacyclophane (**3a**) generated by thermolysis of its precursor tetramethylene Dewar benzene, gave its *ortho*-isomer **5a** in the presence of a small amount (2 mole %) of *p*-toluenesulfonic acid.[6]

In this paper, proton affinities (PA), strain energies (SE), and enthalpies of formation (ΔH^0_f) have been obtained by MNDO and MINDO/3 calculations on the species presented in Scheme 2. It is shown that a qualitative reasoning in terms of PA, SE or ΔH^0_f explains the observed differences in chemical behavior. The calculated gas phase data are corrected for the



Scheme 2

liquid phase in order to obtain a better basis for correlation of the calculated and experimental data, especially for a direct comparison between neutral species and ions. Finally, the experimental gap concerning the behavior of **1b** has been closed.

CALCULATIONS

As starting geometries, those obtained by MM-2 calculations were used. The input data were generated graphically and care was taken that all following calculations were performed on the lowest energy conformer. All compounds were calculated with standard MNDO[10] and MINDO/3[11] programs from MOPAC;[12] the calculations were run on a VAX 11/785. All structures were fully optimized for all geometrical variables with the standard DFP algorithm. Since it is well known that MNDO performs better on ground state neutrals and MINDO/3 gives better results for ground state ions,[13] both methods were applied for all species calculated (Table 1). The gas phase proton affinities were calculated according to equation (1) (B = benzene derivative).

$$\mathrm{PA} = \Delta H^0_f(\mathrm{B}) + \Delta H^0_f(\mathrm{H}^+) - \Delta H^0_f(\mathrm{HB}^+) \qquad (1)$$

The experimental value of $\Delta H^0_f(\mathrm{H}^+)$ was used (367·2 kcal mol^{-1})[14] because both MNDO and MINDO/3 predict $\Delta H^0_f(\mathrm{H}^+)$ to be too high. Strain energies for the neutral compounds were calculated by equation (2).

$$\mathrm{SE} = \Delta H^0_f(\mathrm{B}) - \Delta H^0_f(\mathrm{B}') \qquad (2)$$

Table 1. Calculated heats of formation of **1**–**6** and **10**–**15** (ΔH^0_f; kcal mol^{-1})

Compd	ΔH^0_f		$\Delta H^0_{f,THF}$[a]	
	MNDO	MINDO/3	MNDO	MINDO/3
1a	93·0[b]	102·6	82·0	91·6
1b	62·5[b]	74·3	51·5	63·3
1c	39·1[b]	49·4	28·1	38·4
2a	226·9	221·7	38·4	48·4
2b		206·4	23·8	33·1
2c	202·2	193·4	13·7	20·1
3a	76·5[c]	88·7	66·1	77·7
3b	45·6[b]	55·0	34·6	44·0
3c	26·6[b]	32·5	15·6	21·5
4a	228·6	225·3	40·1	52·0
4b	210·7	205·8	22·2	32·5
4c	204·2	195·6	15·7	22·3
5a	1·5	12·9	−9·5	1·9
5b	1·9	10·3	−9·1	−0·7
5c	2·4	7·8	−8·6	−3·2
6a	195·9	187·5	7·4	14·2
6b	195·0	184·1	6·5	10·8
6c	200·3	187·2	11·8	13·9
10	5·6	16·2	−4·2	6·4
11	194·4	189·8	5·9	16·5
12	5·9	16·4	−3·1	7·4
13	196·8	193·2	8·3	19·9
14	8·4	19·6	−1·6	9·6
15	197·7	193·3	9·2	20·0

[a] According to equation (6)
[b] From Reference 7
[c] From Reference 34

where $\Delta H^0_f(\mathrm{B}')$ is the value obtained from Benson's standard group increments[15] without incorporation of ring strain contributions. For the charged species, an extra correction was necessary for the calculation of their SE's (equation (3)).

$$\mathrm{SE} = \Delta H^0_f(\mathrm{BH}^+) - \Delta H^0_f(\mathrm{B}') - [\Delta H^0_f(\text{xylene H}^+) - \Delta H^0_f(\text{xylene})] \qquad (3)$$

The last term in this equation accounts for the electrostatic contribution, the substitution pattern and the enthalpy of formation of the additional C—H bond. The SE of the cyclophane derivatives **2**, **4** and **6** was calculated using the xylene derivatives **11**, **13** and **15**, respectively. Table 2 shows that the SE's for the neutral *ortho*-isomers (**5a**–**c**) do not differ significantly from those of the corresponding simple cycloalkenes[15] ($|\overline{\Delta \mathrm{SE}}| = 3{\cdot}1$ and 6·4 kcal mol^{-1} for MNDO and MINDO/3, respectively). In the case of the protonated *ortho*-isomers (**6a**–**c**), the mean absolute differences compared to those of the corresponding cycloalkanes (chosen as reasonable models for the cycloalkyl cations)[15] ($|\overline{\Delta \mathrm{SE}}| = 2{\cdot}7$ and 7·4 for MNDO and MINDO/3 respectively) are of the same magnitude. This suggests that the computation of SE's for protonated compounds via equation (3) gives reasonable values.

The largest objection against such analyses of reaction behavior is the comparison of gas phase data (calculations) with liquid phase experimental results. As can be seen from Table 1, the positively charged compounds have a high ΔH^0_f caused by an electrostatic contribution

Table 2. Strain energies (SE) and proton affinities (PA) of **1**–**6** and **10**–**15** (kcal mol^{-1})

Compd	SE[a]		PA[b]		pK_B[c]	
	MNDO	MINDO/3	MNDO	MINDO/3	MNDO	MINDO/3
1a	88·4[d]	98·0	233·3	248·1	−37·7	−37·0
1b	62·9[d]	74·6	217·5	235·1	−24·0	−26·1
1c	44·4[d]	54·7	204·1	223·2	−12·5	−15·8
2a	33·5	43·5				
2b	23·7	33·1				
2c	18·7	25·5				
3a	71·9[e]	84·1	215·7	230·6	−22·5	−22·2
3b	46·1[d]	55·3	202·2	216·4	−10·7	−9·9
3c	31·9[d]	37·8	194·5	204·1	−4·2	−0·7
4a	33·1	43·9				
4b	20·1	29·3				
4c	18·6	24·1				
5a	−3·1	8·3	172·8	192·6	14·6	10·6
5b	2·3	10·7	174·1	193·4	13·5	9·9
5c	7·7	13·1	169·3	187·8	17·6	14·8
6a	1·6	9·2				
6b	6·5	10·7				
6c	16·3	18·8				
10			178·4	183·0	8·7	8·7
11						
12			176·3	179·9	9·9	10·8
13						
14			175·5	179·9	9·3	8·8
15						

[a] According to equations (2) and (3)
[b] $\Delta H^0_f(H^+) = 367{\cdot}2$ kcal mol^{-1}, see equation (1)
[c] According to equation (9c)
[d] Taken from Reference 7
[e] Calculated from Reference 34

which would be much smaller in solution due to polarization and solvation. This makes direct comparison with experimental results difficult. It is known that MNDO and MINDO/3 predict PA's well for many compounds.[10,16] The only experimental liquid phase results on PA's are those of Mackor *et al.*[17] They measured the enthalpy of reaction ΔH^0_r for the protonation reaction of benzene derivatives (B) in HF (equation (4)),

$$B_{HF} + HF_{HF} \rightarrow BH^+_{HF} + F^-_{HF} \tag{4}$$

which leads to equation (5):

$$\Delta H^0_r = -\Delta H^0_f(B_{HF}) - \Delta H^0_f(HF_{HF}) + \Delta H^0_f(F^-_{HF}) + \Delta H^0_f(BH^+_{HF}) \tag{5}$$

With the known values of the terms in equation (5)[17] and estimated enthalpies of transfer (ΔH^0_{transf}) for these species from HF to THF, this equation can be used to estimate the enthalpy of transfer (ΔH^0_{transf}) for the charged compounds from the gas phase to a solution state in THF; as derived in Appendix 1, this leads to equation (6),

$$\Delta H^0_f(BH^+) + \Delta H^0_{transf} = \Delta H^0_f(BH^+_{THF}) \tag{6}$$

with $\Delta H^0_{\mathrm{transf}} = -188{\cdot}5\,\mathrm{kcal\,mol^{-1}}$ for MNDO and $\Delta H^0_{\mathrm{transf}} = -173{\cdot}3\,\mathrm{kcal\,mol^{-1}}$ for MINDO/3 (Appendix 1).

For the neutral compounds, the calculated gas phase values need to be corrected by the enthalpies of vaporization (ΔH^0_{v}) and enthalpies of solution (ΔH^0_{s}, see Appendix 1) according to equation (7).

$$\Delta H^0_{\mathrm{f}}(\mathrm{B_{THF}}) = \Delta H^0_{\mathrm{f}}(\mathrm{B}) - \Delta H^0_{\mathrm{v}} + \Delta H^0_{\mathrm{s}} \qquad (7)$$

A compilation of $\Delta H^0_{\mathrm{f,THF}}$ is given in Table 1. The values of $\Delta H^0_{\mathrm{f,THF}}$ can now be used to calculate $\mathrm{p}K_{\mathrm{B}}$ values with the aid of equations (8) and (9).

$$\Delta G^0 = -RT\ \ln K_{\mathrm{B}} \qquad (8)$$

which leads to equation (9a)

$$\mathrm{p}K_{\mathrm{B}} = \frac{\Delta G^0(\mathrm{BH^+{}_{THF}}) - \Delta G^0(\mathrm{B_{THF}}) - \Delta G^0(\mathrm{H^+{}_{THF}})}{2{\cdot}3RT} \qquad (9a)$$

This reduces to equation (9b) because of the convention that $\Delta G^0(\mathrm{H^+{}_{THF}}) = 0$ (see Appendix 1).

$$\mathrm{p}K_{\mathrm{B}} = \frac{\Delta G^0(\mathrm{BH^+{}_{THF}}) - \Delta G^0(\mathrm{B_{THF}})}{2{\cdot}3RT} \qquad (9b)$$

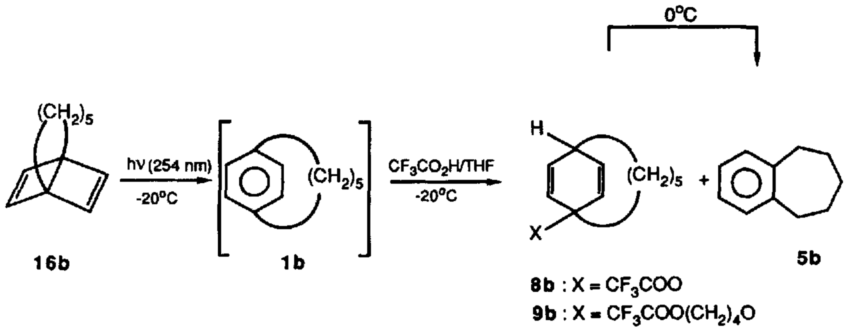
If we assume that the entropy contributions $\Delta S^0(\mathrm{BH^+{}_{THF}})$ and $\Delta S^0(\mathrm{B_{THF}})$ do not differ much between the species in the series considered here, the unknown $\Delta\Delta S^0$ is approximately constant. Thus, the available $\Delta H^0_{\mathrm{f,THF}}$ can be used as an approximation, and equation (9b) is transformed to equation (9c) which gives a *relative* $\mathrm{p}K_{\mathrm{B}}$ scale (see Table 2).

$$\mathrm{p}K_{\mathrm{B}} = \frac{\Delta H^0(\mathrm{BH^+{}_{THF}}) - \Delta H^0(\mathrm{B_{THF}})}{2{\cdot}3\mathrm{RT}} \qquad (9c)$$

The reliability of these $\mathrm{p}K_{\mathrm{B}}$ values can be estimated as follows. Possible errors in the calculations stem from the estimated values for the enthalpies of transfer from HF to THF and particularly from the uncertainty of the MNDO and MINDO/3 calculational results for ΔH^0_{f}; they are estimated to be in the order of approximately 5–10 kcal mol^{-1}.[16] Calibration for **10** of the experimental value ($\mathrm{p}K_{\mathrm{B}}(\mathbf{10}_{\mathrm{HF}}) = 5{\cdot}7$)[17] with the calculated one ($\mathrm{p}K_{\mathrm{B}}(\mathbf{10}_{\mathrm{THF}}) = 8{\cdot}7$) for MNDO and MINDO/3 shows that both values agree reasonably within the uncertainty limits of the calculations. It should be pointed out, that the uncertainty in the calculations within a series of compounds is much smaller.

EXPERIMENTAL INVESTIGATION OF [5]PARACYCLOPHANE (1b)

In order to broaden the experimental base for checking the calculational results, it was decided to investigate the 'missing link', i.e. the behavior of **1b** towards acid under carefully controlled conditions. Addition of trifluoroacetic acid during the irridiation of the Dewar isomer **16b** (Scheme 3) ([D$_8$]THF, 254 nm, −20 °C) leads to an increase in the benzocycloheptene **5b**, but when the reaction was monitored by low temperature ^{1}H-NMR, the formation of intermediate addition products **8b** and **9b** was observed; after 5 hours, the product mixture contained **16b**:**8b**:**9b**:**5b** in the ratio 30:20:15:35. The products **8b** and **9b** showed a characteristic AB

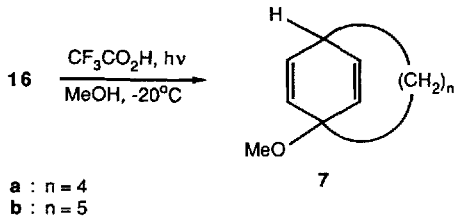


Scheme 3

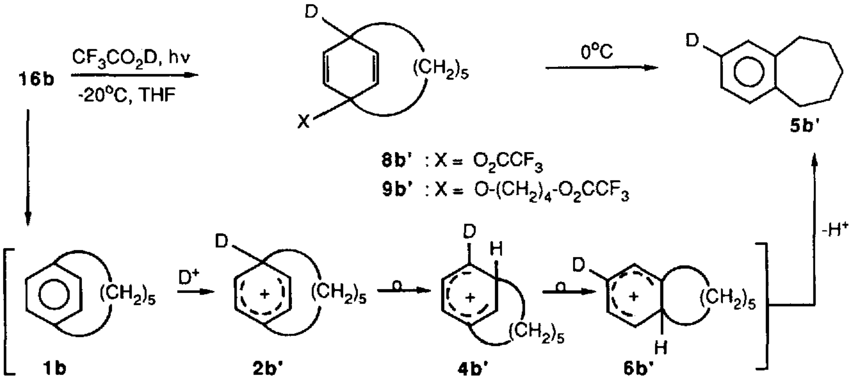
pattern in the olefinic region (**8b**: $\delta_A = 6{\cdot}03$, $\delta_B = 6{\cdot}10$, $J_{AB} = 10\,\text{Hz}$; **9b**: $\delta_A = 5{\cdot}74$, $\delta_B = 5{\cdot}81$, $J_{AB} = 10\,\text{Hz}$), similar to that of the isolable compounds **8a** and **9a**[4] (**8a**: $\delta_A = 6{\cdot}03$, $\delta_B = 6{\cdot}11$, $J_{AB} = 10\,\text{Hz}$; **9a**: $\delta_A = 5{\cdot}86$, $\delta_B = 6{\cdot}05$, $J_{AB} = 10\,\text{Hz}$). Compounds **8b** and **9b** were unstable above 0 °C and reacted to give **5b**, so that they could not be isolated.

During the irradiation of **16b**, **8b** was formed faster than **9b**; their final ratio was 60 : 40 (see Experimental Section). This means that under our conditions, trifluoracetic acid and/or its anion reacts faster than the more abundant, but weaker nucleophile THF (cf. Scheme 1). Warming the solution to 0 °C caused **8b** to decompose to **5b** faster than **9b** did. This is a consequence of the better leaving group of **8b** ($X = O_2CCF_3$) compared to that of **9b** ($X = O(CH_2)_4O_2CCF_3$). When Dewar benzene **16b** was photolyzed at 0 °C in methanol, the major product formed was the methanol adduct **7b** (88%) besides some **5b** (12%) (Scheme 4), in line with the superior basicity of methanol.

Details of the mechanism for the rearrangement of **1b** to **5b** by acid were revealed by subjecting **16b** in [D$_8$]THF to photolysis at −20 °C in the presence of CF_3CO_2D, followed by warming to 0 °C (Scheme 5). We obtained quantitatively **5b′** which was deuterated exclusively at the β-position as was established by ^{2}H-NMR spectroscopy; the detection limit for α-deuteration is about 5%. The chemical shifts of ^{1}H or ^{2}H at the α or β position of **5b′** are identical, but the ^{2}H-NMR spectrum showed a characteristic triplet pattern for a β-deuterated compound ($^3J(\text{HD}) = 1{\cdot}1\,\text{Hz}$). Deuteration of **1b** at the *ipso*-position leads to **2b′** (Scheme 5) which rearranges to **4b′**. If in the ensuing step, **4b′** would deprotonate and subsequently again add a deuteron, two deuteriums would have been incorporated; eventually, a doubly deuterated **5b** would result which is easily recognized by its characteristic ^{2}H-NMR spectrum. This was not observed. If, on the other hand, **2b′** rearranges to **5b′** via two consecutive



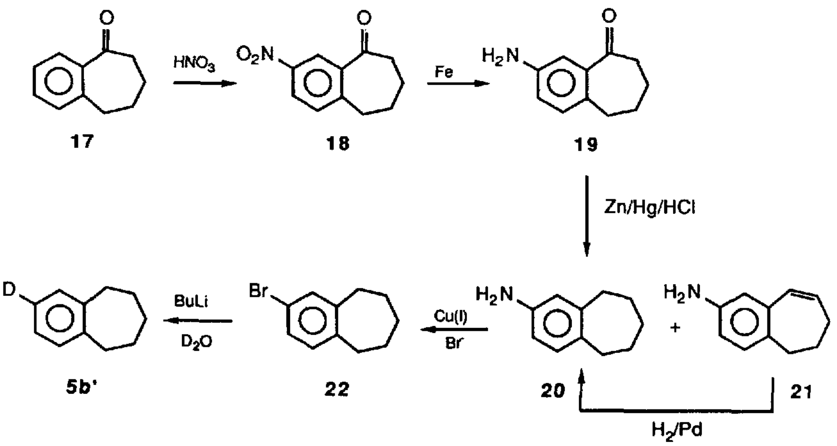
Scheme 4



Scheme 5

1,2-carbon shifts without intermediate deprotonation, only one deuterium is incorporated into the β-position in agreement with experiment. Therefore, our result reveals the same two-step mechanism for **1b** as already found for **1c** (see Introduction), the difference being that for reasons of higher strain, **4b** is completely converted to **6b** (and hence yields **5b**), while the rearrangement of **4c** to **6c** is apparently slower and competes with deprotonation to **3c**.[8a]

In order to confirm the structure of **5b′**, we performed an independent synthesis, which is shown in Scheme 6; this sequence was performed only once and was not optimized. Nitration of α-benzosuberone (**17**) at −10 °C yielded predominantly the β-isomer **18** (35%)[18] which was separated by crystallization and reduced by iron in glacial acetic acid to the amino compound **19**.[19] Clemmensen reduction[20] of **19** gave two products **20** and **21** which, without separation, were hydrogenated over Pd/C to **20** in low yield (9%). After diazotization[21] and bromination, the β-bromobenzocycloheptene (**22**) was isolated by preparative GLC (14%). All intermediates (**18**, **19**, **20**, and **22**) were shown to be the β-isomers by ^{1}H-NMR spectroscopy (one *ortho* and one *meta* coupling was observed, see Experimental). By means of ^{13}C-NMR spectroscopy it could also be established that in **18** and **19** the substituent was attached to the



Scheme 6

3-position, and thus in **20** and **22** to the 2-position ($|\overline{\Delta\delta}|_{\beta} \leq 1$ ppm, as contrasted by $|\overline{\Delta\delta}|_{\alpha} \geq 3$ ppm, in comparison with shifts calculated from increments[22]). Finally, lithiation of **23** with *n*-butyllithium followed by quenching with D_2O gave **5b**′ (80% yield, 86% D incorporation). ^2H- and ^{13}C-NMR spectra were identical with those of **5b**′ obtained from the photolysis experiments.

DISCUSSION

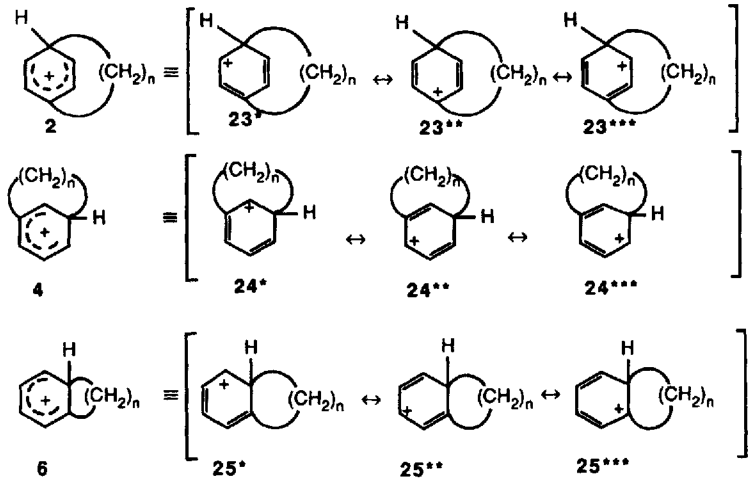
Formation and rearrangement of protonated paracyclophanes 2

The key step in the acid catalyzed rearrangement of the [*n*]paracyclophanes **1a–c** is the first protonation at an *ipso*-position to yield **2a–c** (Scheme 1). This reaction is accompanied by a considerable decrease in SE (Table 2); it varies from 54·9 kcal mol^{-1} (**2a**) via 39·2 kcal mol^{-1} (**2b**) to 25·7 kcal mol^{-1} (**2c**) (MNDO). Also, the highly negative values of pK_B (Table 2: −37·0 (**1a**), −26·1 (**1b**), −15·8 (**1c**) MINDO/3 are remarkable. Even keeping the large uncertainty limits in mind, they tell us that the small paracyclophanes are extremely strong bases, or put the other way round, their conjugate acids **2** are extremely weak acids: pK_A = +37 for **2a**, a *protonated* benzenoid aromatic. This acidity is intermediate between that of (neutral !) diphenylmethane and toluene or, switching back to the basicity scale, **1a** is a stronger base than the diphenylmethyl anion !! Of course, this high basicity does not so much originate from electronic properties, but is due to energy gain by release of strain and, for that matter, holds only for protonation at one of the *ipso*-carbons.

Protonation at an *ortho*-position is unfavorable for two reasons. In the first place, it does not release as much strain.[23a] The relation between SE and the basicity constant pK_B is clearly seen from Table 2. The release of strain energy from **1** → **2** decreases with increasing bridge length (**a** → **c**); this makes the protonation reaction less exothermic in this sequence: the pK_B values show a dramatic decrease of 25 pK_B units from **a** → **c**. The reactivity towards acid is also shown by the $\Delta H^0_{f,THF}$ values, equations (6,7), which show that the reaction **1** → **2** is highly exothermic (Table 1; $\Delta H^0_{r,THF} = -43{\cdot}6$ or $-43{\cdot}2$ kcal mol^{-1} for **1a** to $\Delta H^0_{r,THF} = -14{\cdot}4$ or $-18{\cdot}3$ kcal mol^{-1} for **1c** in MNDO and MINDO/3, respectively, see Appendix 1). Secondly, *ortho*-protonation does not lead to a chemical reaction because a 1,2-shift of the bridge cannot take place directly. The order of reactivity (**1a** > **1b** > **1c**) can thus be explained in terms of SE, pK_B or $\Delta H^0_{f,THF}$. This reactivity scale can even be extended to [8]paracyclophane, a molecule which is less strained than **1c**, and therefore reacts only under relatively severe conditions ($AlCl_3$/HCl) to give [8]metacyclophane and octahydrobenzocyclodecene in the ratio 4 : 1.[24]

In terms of qualitative resonance theory, **2** may be described as a mesomeric hybrid composed of the valence bond structures **23*–23***** (Scheme 7). It is clear from both bond orders and charge densities (Table 3, Appendix 2) that structure **23**** is more important in **2a** ($q_{2,6} = 0{\cdot}095$, $q_4 = 0{\cdot}340$) whereas the two equivalent structures **23*** and **23***** make a relatively larger contribution in **2b** ($q_{2,6} = 0{\cdot}119$, $q_4 = 0{\cdot}298$) and **2c** ($q_{2,6} = 0{\cdot}129$, $q_4 = 0{\cdot}276$), because their ‘*anti*-Bredt’ character is less unfavorable due to the bridges being larger. Compound **2c** resembles protonated *p*-xylene (**11**) in terms of charges and bond orders (Table 6, Appendix 2) ($q_{2,6} = 0{\cdot}142$, $q_4 = 0{\cdot}244$).

Once formed, **2** has the option of either adding a nucleophile or rearranging to **4**. The difference in reaction mode between **2a–c** cannot be ascribed to thermodynamic factors, as for all compounds there is hardly any change in stability on going from **2** to **4**. Therefore the



a : n=4; b : n=5; c : n=6

Scheme 7

differences must have a kinetic reason. An important factor may be the charge distribution in **2**. For the Wagner–Meerwein 1,2-shift in **2** to occur, it is necessary to have a positive charge at the *ortho*-position (C-2 or C-6). In the sequence **2a**, **2b**, **2c**, **11**, the charge at the *ortho*-position increases by 37% (MNDO) or 33% (MINDO/3), while at the *para*-position a decrease of 19% (MNDO) or 14% (MINDO/3) is calculated. We believe that in **2a**, the relatively low positive charge at C-2 slows down the rate of the Wagner–Meerwein shift, while at the same time, the higher positive charge at C-4 increases the reactivity towards nucleophiles at that position. Both factors combine to prevent the usual 1,2-rearrangement. In **2c** with its 'normal' charge distribution, the rearrangement to **4c** occurs in the expected fashion. Ion **2b** takes an intermediate position with regard to charge distribution and, as a consequence, shows both reaction modes: in THF, it gives a mixture of **5b** and **8b**/**9b**.

Another factor which one feels intuitively might influence the propensity to 1,2-carbon migration is a geometrical one, i.e. the dihedral angle between the empty *p*-orbital in **23*** and the migrating carbon—carbon bond: if large, it would decrease the reaction rate. A good approximation of the direction of the empty *p*-orbital at the *ortho*-position is that it makes equal angles with all three neighboring bonds. The dihedral angle between the orginal carbon—carbon bond and the *p*-orbital has thus been calculated. This angle does not vary much, but it increases slightly from **2a** → **2b** → **2c** (MNDO: 5; 5; 17 degrees, MINDO/3: 1; 11; 20 degrees, respectively). From this analysis, one would predict a decreasing rate for the Wagner–Meerwein shift in the series **2a** → **2c**, while experimentally we observe that the yield of Wagner–Meerwein product increases in this sequence. This indicates that the geometric factor of orbital alignment cannot be of major importance in the present case, and we therefore feel that the charge distribution is the dominant factor governing product formation.

In a recent paper by Tobe *et al.*, the protonation of (*Z*)[6]paracycloph-3-ene in methanol is reported.[8b] In this case both addition of methanol (leading to the equivalent of **7b**, Scheme 4) and rearrangement to [6]metacycloph-3-ene is observed in a ratio of 5:3. This result fits nicely with preliminary calculations.[23b] Introduction of a double bond in the hexamethylene bridge leads to a strain situation and consequently to a charge distribution intermediate between that of [5]paracyclophane (**1b**) and [6]paracyclophane (**1c**). Therefore, it is not surprising that its chemical behavior also lies between that of **1c** (no reaction in acidic methanol)[8b] and **1b** (formation of **7b** as the major product).

Finally, it should be pointed out that *ipso*-protonations have been invoked before to explain the reactivity of [2.2]paracyclophane systems.[25]

Rearrangements of protonated metacyclophanes 4

In line with the discussion presented above, **4**, the intermediate cations formed from **2**, can be described as a mesomeric hybrid of three resonance structures **24***–**24***** (see Scheme 7). From Table 4 (Appendix 2) it can be seen that shortening of the bridge makes structure **24*** increasingly dominant. The violation of Bredt's rule is more severe in **24**** and **24***** than in **24***. Comparison with reference structure **13** (Scheme 2; Table 6, Appendix 2) reveals that **4c** is more or less a normal protonated aromatic compound; although the bond orders differ slightly, bond distances are almost equal.

The cations **4** can either lose a proton to form **3** or undergo a Wagner–Meerwein shift to yield the *ortho*-isomers **6**. The $\Delta H^0_{\mathrm{r,THF}}$ (see equation (18) and Table 1) indicate that the formation of **6** is exothermic by 4–38 kcal mol^{-1} which is mainly due to release of strain energy. On the other hand, deprotonation is endothermic by about -1 to 26 kcal mol^{-1} and is obviously dominated by the increase of strain energy in this reaction.

The observation that **4c** rearranged to **6c** but also deprotonated to **3c** is qualitatively explained by the calculational results. The deprotonation step from **4c** to **3c** is exothermic by 0·7 kcal mol^{-1} in MINDO/3 while MNDO predicts the reaction to be almost thermoneutral. In both calculational methods, the rearrangement to **6c** is clearly exothermic (4–9 kcal mol^{-1}); this is qualitatively reflected in the observed product ratio of **3c**:**6c** = 1:3,[8a] although the correlation is far from quantitative. On the other hand, the calculations correctly predict the exclusive rearrangement reaction of **4b** to **6b** ($\Delta H^0_{\mathrm{r,THF}} = -15{\cdot}7$ kcal mol^{-1} and $-21{\cdot}7$ kcal mol^{-1} for MNDO and MINDO/3, respectively); the deprotonation step **4b** → **3b** ($\Delta H^0_{\mathrm{r,THF}} = 12{\cdot}4$ and 11·5 kcal mol^{-1} for MNDO and MINDO/3) is highly unfavorable in this case. This means that the reverse reaction of **3b** via **4b** to **6b** is quite favorable and it is indeed observed experimentally.[9] Although the conditions under which **3a** reacts with acid (generation of **3a** by thermolysis of its corresponding Dewar isomer at 150 °C in the presence of 2 mole % acid) are quite different compared to those of **3b** and **3c**, it, too, protonates to give **4a** which then rearranges via **6a** to give **5a**.[6]

Protonated orthocyclophanes 6

The last step in the reaction sequence is a deprotonation reaction of the benzenonium ions **6**. This deprotonation step comprises the formation of neutral aromatic molecules **5**, and is accompanied by a slight decrease in strain energy; it is exothermic by *ca.* 10–20 kcal mol^{-1}. Comparison of **6** with their corresponding xylene derivative **15** reveals a close correspondence in bond orders and charge distributions (Tables 5,6).

CONCLUSIONS

The results present additional evidence for the mechanism of conversion of **1** to **5**; it consists of *ipso*-protonation, followed by two consecutive 1,2-carbon shifts and finally deprotonation.

The overall driving force for these rearrangements is the release of strain energy present in these molecules. The calculations show that most of this strain release is realised in the first step, i.e. protonation at the *ipso*-position in **1** to yield **2**. Both MNDO and MINDO/3 calculations are capable of giving a qualitatively correct description of the observed reactions. They predict the right order of reactivity towards acid on the basis of PA, SE and $\Delta H^0{}_{f,THF}$, and the formation of the addition products, on the basis of differences in charge densities. In particular, the striking difference in reaction pattern between [4]- and [6]paracyclophane (**1a** and **1c**, respectively) can be explained, as well as the intermediate behavior of [5]paracyclophane (**1b**). Although many assumptions have been made in the calculation of $\Delta H^0{}_{f,THF}$ of the intermediate ions, these values are consistent with the observed facts and thus allow a direct comparison of neutral and positively charged species in solution.

EXPERIMENTAL SECTION

NMR spectra were measured on a Bruker WM-250 spectrometer; residual solvent proton signals were used as internal standard. Assignments marked with * or ** may have to be reversed. GCMS spectra were measured on a HP 5890 MSD and HRMS spectra on a Varian CH-5 DF operating at 70 eV. Preparative GLC was performed on an Intersmat 120 (1·5 m column, 13% SE-30, 60 ml H_2/min) and MPLC was performed with an Jobin Yvon miniprep LC. Irradiations were performed in a Rayonet photochemical reactor with a merrygoround installation of the light source (λ = 254 nm).

3-Nitro-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-5-one (18)

To 55 ml of concentrated H_2SO_4 cooled to −10 °C, 24·7 g (0·15 mol) of **17** was added. In 3·5 hours a mixture of 20 ml conc. HNO_3 and 45 ml conc. H_2SO_4 was added and care was taken that the temperature did not rise above −10 °C. After an additional 15 min the mixture was poured on ice, separated and titrurated with hot $CHCl_3$. The organic phase was washed twice with a $NaHCO_3$ solution, once with brine dried with $MgSO_4$ and concentrated under reduced pressure to give 11·1 g (54 mmol, 35%) of yellow crystals of **18**, m.p. 90–91 °C (EtOH). ^{1}H-NMR (250·1 MHz, $CDCl_3$, 295K): δ 8·55 (d, J = 2·5 Hz, 1H, H(4), 8·25 (dd, J = 2·5, 8·1 Hz, 1H, H(2)), 7·40 (d, J = 8·1 Hz, 1H, H(1), 3·05 (t, J = 6.2 Hz, 2H, H(6), 2·80 (m, 2H, H(9)), 1·92 (m, 4H, H(7,8)). ^{13}C-NMR (62·9 MHz, $CDCl_3$, 295K): δ 203·4 (s, C(5)), 148·1 (s, C(9a)), 147·0 (s, C(3)), 139.8 (s, C(4a)), 131·0 (d, $^1J_{CH}$ = 163 Hz, C(1)), 126·2 (d, $^1J_{CH}$ = 171 Hz, C(2), 123·8 (d, $^1J_{CH}$ = 170 Hz, C(4)), 40·5 (t, $^1J_{CH}$ = 128 Hz, C(6)), 32·5 (t, $^1J_{CH}$ = 128 Hz, C(9)), 24·8 (t, $^1J_{CH}$ = 130 Hz, C(7)*), 20·7 ($^1J_{CH}$ = 130 Hz, C(8)*). MS: m/z = 205 (100%, $M^{+\cdot}$), 188 (52%), 176 (49%), 163 (46%), 131 (44%), 103 (39%), 91 (39%). HRMS ($C_{11}H_{11}NO_3$): Calcd. 205·0739, Found 205·0744.

3-Amino-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-5-one (19)

To a mixture of 80 ml glacial acetic acid and 16 ml H_2O at 90–95 °C was added 8·22 g (40 mmol) of **18**. In 75 min 10·7 g (0·19 mol) of Fe powder was added. After the first 45 min an extra amount of 25 ml H_2O was added to the mixture. When the addition of Fe was complete, the mixture was heated for 45 min after which H_2O and hyflo were added and filtered off. The filtrate was extracted three times with ether and the combined organic layers were washed with

$HaHSO_3$, twice with H_2O, dried over $MgSO_4$ and concentrated at reduced pressure. The residue (5·5 g) was chromatographed by MPLC (40% pentane, 60% EtOAc, silicagel 60, 15 μm) and gave 2·56 g (14·6 mmol, 36%) of **19** as a colourless oil. ^{1}H-NMR (250·1 MHz, $CDCl_3$, 295K): δ 7·06 (d, J = 2·6 Hz, 1H, H(4)), 7·00 (d, J = 7·8 Hz, 1H, H(1)), 6·76 (dd, J = 2·6, 7·8 Hz, 1H, H(2)), 3·69 (bs, 2H, NH_2), 2·83 (t, J = 6·1 Hz, 2H, H(6)), 2·71 (m, 2H, H(9)), 1·82 (m, 4H, H(7,8). ^{13}C-NMR (62·89 MHz, $CDCl_3$, 295K): δ 205·9 (s, C(5)), 144·9 (s, C(3)), 139·4 (s, C(4a)), 131·6 (s, C(9a)), 130·8 (d, $^1J_{CH}$ = 158 Hz, C(1)), 118·9 (d, $^1J_{CH}$ = 157 Hz, C(2)), 114·6 (d, $^1J_{CH}$ = 158 Hz, C(4)), 40·9 (t, $^1J_{CH}$ = 128 Hz, C(6)), 31·7 (t, $^1J_{CH}$ = 128 Hz, C(9)), 25·5 (t, $^1J_{CH}$ = 128 Hz, C(7)*), 21·0 (t, $^1J_{CH}$ = 131 Hz, C(8)*). MS: m/z = 175 (100%, $M^{+\cdot}$), 146 (48%), 119 (100%), 106 (51%). HRMS ($C_{11}H_{13}NO$): Calcd. 175·0997, Found 175·1012.

2-Amino-6,7,8,9-tetrahydro-5*H*-benzocycloheptene (20)

A mixture of 7·5 g (0·11 mol) Zn, 0·6 g (2 mmol) $HgCl_2$, 8 ml H_2O and 0·35 ml conc. HCl was stirred for 10 minutes and the aqueous solution was decanted. To this amalgam, 6·5 ml conc. HCl, 5 ml H_2O, 5 ml toluene and 2·1 g (12 mmol) of **19** were added and the resulting mixture was heated to reflux for 19 hours, with addition of an extra portion of 3 ml conc. HCl after 3·5 and 17 hours. The water–toluene mixture was decanted and extracted twice with Et_2O. The organic phase was washed twice with $NaHCO_3$ solution, once with H_2O, dried on $MgSO_4$ and concentrated under reduced pressure. The residue was dissolved in 45 ml EtOH and hydrogenated with 0·5 g Pd/C (10%). After addition of H_2O and hyflo the solution was filtered and extracted twice with ether. The dried and concentrated organic phase was chromatographed (MPLC, gradient elution: 20% EtOAc/pentane – 50% EtOAc/pentane, silicagel 60, 15 μm) and gave 0·2 g (1 mmol, 9%) **20** as a colourless oil. ^{1}H-NMR (250·1 MHz, $CDCl_3$, 295K): δ 6·91 (d, J = 7·6 Hz, 1H, H(4)), 6·51 (d, J = 2·4 Hz, 1H,H(1)), 6·45 (dd, J = 2·4, 7·6 Hz, 1H, H (3)), 3·54 (bs, 2H, NH_2), 2·65 (m, 4H, H(5,9)), 1·75 (m, 2H, H(7)), 1·65 (m, 4H, H(6,8)). ^{13}C-NMR (62·89 MHz, $CDCl_3$, 295K): δ 144·3 (s, C(2)), 144·2 (s, C(9a)), 133·7 (s, C(4a)), 129·7 (d, $^1J_{CH}$ = 154 Hz, C(4)), 116·4 (d, $^1J_{CH}$ = 153 Hz, C(1)), 112·2 (d, $^1J_{CH}$ = 156 Hz, C(3)), 36·8 (t, $^1J_{CH}$ = 125 Hz, C(9)*), 35·8 (t, $^1J_{CH}$ = 125 Hz, C(5)*), 32·7 (t, $^1J_{CH}$ = 130 Hz, C(7)), 28·9 (t, $^1J_{CH}$ = 126 Hz, C(8)**), 28·4 (t, $^1J_{CH}$ = 128 Hz, C(6)**). MS: m/z = 161 (100%, $M^{+\cdot}$), 146 (26%), 132 (86%), 120 (31%). HRMS ($C_{11}H_{15}N$): Calcd. 161·1204, Found 161·1191.

2-Bromo-6,7,8,9-tetrahydro-5*H*-benzocycloheptene (22)

To a solution of 0·4 ml 48% HBr at 0 °C was added 0·1 g (0·7 mmol) **20** followed by 70 μl of a solution of $NaNO_2$ (11 M). The mixture was stirred for a half hour; then the temperature raised to room temperature and 3 mg Cu was added. The resulting mixture was stirred for 2 hours at 0 °C and for a half hour at room temperature, after which 5 ml of H_2O was added. The mixture was extracted three times with CH_2Cl_2 and the combined organic phases were washed twice with a $NaHCO_3$ solution, once with H_2O, dried on $MgSO_4$ and concentrated at reduced pressure to give a crude yield of 0·08 g. Final purification by GLC gave 21 mg (0·09 mmol = 14%) of **22** as a colourless liquid. ^{1}H-NMR (250·1 MHz, $CDCl_3$, 295K): δ 7·25 (d, J = 2·1 Hz, 1H, H(1)), 7·20 (dd, J = 2·1, 7·8 Hz, 1H, H(3)), 6·96 (d, J = 7·8 Hz, 1H, H(4)), 2·75 (m, 4H, H(5,9)), 1·82 (m, 2H, H(7)), 1·64 (m, 4H, H(6,8)). ^{13}C-NMR (62·89 MHz, $CDCl_3$, 295K): δ 145·7 (s, C(2)), 142·4 (s, C(4a)), 131·7 (d, $^1J_{CH}$ = 161 Hz, C(1)), 130·6 (d, $^1J_{CH}$ = 159 Hz, C(4)), 128·6 (d, $^1J_{CH}$ = 166 Hz, C(3)), 119·2 (s, C(9a)), 36·4 (t, $^1J_{CH}$ = 127 Hz, C(9)*), 36·1 (t, $^1J_{CH}$ = 126 Hz, C(5)*), 32·5 (t, $^1J_{CH}$ = 127 Hz, C(7)), 28·1 (t, $^1J_{CH}$ = 127 Hz, C(6,8)). MS: *m/z* = 226 (39%, $M^{+\cdot}$), 224 (39%), 145 (100%), 115 (35%). HRMS ($C_{11}H_{13}{}^{81}Br$): Calcd. 226·0182, Found 226·0156.

[2-D]-6,7,8,9-tetrahydro-5*H*-benzocycloheptene (5b′)

To a cooled solution (−60 °C) of 17 mg (0·07 mmol) **22** in 0·6 ml Et_2O 0·5 ml *n*-BuLi (1·56 M in hexane) was added. The mixture was stirred 15 min at −50 °C and 15 min at room temperature after which 25 µl D_2O was added. After a threefold extraction with Et_2O, the combined organic phases were dried and concentrated and gave 9 mg (0·06 mmol, 80%) **5b′** (86% deuterium incorporated). ^{1}H-NMR (250·1 MHz, $CDCl_3$, 295K): δ 7·10 (s, 3H, Aryl-H), 2·80 (m, 4H,H (5,9)), 1·83 (m, 2H, H(7)), 1·66 (m, 4H, H(6,8)). ^{13}C-NMR (62·89 MHz, $CDCl_3$, 295K): δ 143·4 (s, C(4a, 9a)), 129·0 (d, $^1J_{CH}$ = 161 Hz, C(1)), 128·8 (d, $^1J_{CH}$ = 161 Hz, C(4)), 125·8 (d, $^1J_{CH}$ = *ca.* 160 Hz, C(2,3)), 36·7 (t, $^1J_{CH}$ = 127 Hz, C(5,9)), 32·8 (t, $^1J_{CH}$ = 135 Hz, C(7)), 28·4 (t, $^1J_{CH}$ = 130 Hz, C(6,8)). ^{2}H-NMR (38·4 MHz, $CHCl_3$, 295K): δ 7·14 (t, $^3J_{HD}$ = 1·1 Hz). MS: *m/z* = 147 (82%, $M^{+\cdot}$), 146 (13%), 132 (43%), 119 (48%), 118 (88%), 105 (100%), 92 (50%). HRMS($C_{11}H_{13}{}^2H$): Calcd. 147·1158, Found 147·1143.

Irradiation of 1,4-pentamethylene Dewar benzene (16b) in the presence of acid

A solution of 10 mg (0·07 mmol) **16b** and 5 µl (0·07 mmol) CF_3CO_2D in [D_8]THF was irradiated for 9 h in a quartz NMR tube at −20 °C with a 254 nm lamp. ^{1}H-NMR spectra were recorded at intervals of two hours and showed the increase of **8b** and **9b**. After 5 hours of irradiation the product distribution between **16b**:**8b**; **9b**:**5b** was 30:20:15:35. Warming the solution to room temperature led to a quantitative rearrangement of **8b** and **9b** to **5b**. No **8b** or **9b** could be isolated. Due to the presence of H_2O in this sample of **16b**, the incorporation of deuterium was only 15%. This also implied that H-7 in **8b** and **9b** could be detected.[4]

1-Trifluoroacetoxybicyclo[5.2.2]undeca-8,10-diene (8b)

^{1}H-NMR (250 MHz, [D_8]THF, 220K): δ 6·65 (AB part of ABX system, δ(A) = 6·03, H(9,10), δ(B) = 6·10, H(8,11)), J_{AB} = 10 Hz, J_{BX} = 4 Hz, 4H), 3·1 (X-part of ABX system, m, 1H, H(7). Other signals coincided with those of **16b** and **5b**.

1′,1′,2′,2′,3′,3′,4′,4′-[D8]-1-(4′-trifluoroacetoxybutoxy)bicyclo[5.2.2.]-undeca-8,10-diene (9b)

^{1}H-NMR (250 MHz, [D_8]THF, 220K): δ 5·75 (AB part of ABX system, δ(A) = 5·74, H(9,10), δ(B) = 5·81, H(8,11), J_{AB} = 10 Hz, J_{BX} = 4 Hz, 4H), 2·9 (m, 1H, X-part of ABX system). Other signals coincided with those of **16b** and **5b**.

Irradiation of 1,4-pentamethylene Dewar benzene (16b) in acidic methanol

A solution of 5 mg (0·03 mmol) **16b** in MeOH in a quartz tube was irradiated at 0 °C for two hours with a low pressure mercury lamp in the presence of 12 µl (5 eq) CF_3CO_2H. The solution was taken up in $CDCl_3$ and the MeOH was extracted with water. The resulting $CDCl_3$ solution contained a mixture of **5b** (12%) and **7b** (88%). At −20°C **7b** rearranged to **5b** within two days. **7b**: ^{1}H-NMR (90 MHz, $CDCl_3$, 293K): δ 5·84 (AB part of ABX system, δ(A) = 6·04, H(8,11), δ(B) = 5·67, H(9,10), J_{AB} = 10 Hz, J_{BX} = 5 Hz, 4H), 3·15 (s, 3H, OMe), 2·95 (m, 1H, H(7), 1·8–1·2 (m, 10H). MS: *m/z* = 178 (2%, $M^{+\cdot}$), 121 (100%), 91 (15%).

SUPPLEMENTARY MATERIAL AVAILABLE

Appendix 2 with Tables 3–6 (selected atomic charges, bond orders, and bond distances of **2**, **4**, **6**, **11**, **13**, and **15** (4 pages)).

APPENDIX 1

Due to the strong hydrogen bonds in HF equation (4) should be written more precisely as equation (10a).

$$B_{HF} + 2\ HF_{HF} \rightarrow BH^+{}_{HF^+} + HF_2{}^-{}_{,HF} \tag{10a}$$

which leads to equation (10b) ($\Delta H^0{}_{r,HF}$ = enthalpy of reaction in HF).

$$\Delta H^0{}_{r,HF} = \Delta H^0{}_f(BH^+{}_{HF} + \Delta H^0{}_f(HF_2{}^-{}_{,HF} - \Delta H^0{}_f(B_{HF}) - 2\Delta H^0{}_f(HF_{HF}) \tag{10b}$$

Unfortunately, the value of $\Delta H^0{}_f$ ($HF_2{}^-{}_{,HF}$) is not known, but the values of $\Delta H^0{}_f$ ($HF_2{}^-$ = −155·1 kcal mol^{-1} and $\Delta H^0{}_f$(HF) = −76·4 kcal mol^{-1} in aqueous solution are known;[26] they can be used as an approximation in equation (10b). If the known terms are substituted in equation (10b), one obtains an experimentally determined enthalpy difference between BH^+ and B. This is exemplified for *p*-xylene (**10**) with the measured $\Delta H^0{}_{r,HF}$ obtained by Mackor *et al.* ($\Delta H^0{}_{r,HF}$ = 3·8 kcal mol^{-1})[17] (equation (11)).

$$\begin{aligned} 3{\cdot}8\,\text{kcal mol}^{-1} &= \Delta H^0{}_f(\mathbf{11}_{HF}) - 155{\cdot}1\ \text{kcal mol}^{-1} \\ &\quad - \Delta H^0{}_f(\mathbf{10}_{HF}) + 2(76{\cdot}4)\ \text{kcal mol}^{-1} \end{aligned} \tag{11a}$$

which simplifies to

$$6{\cdot}1\ \text{kcal mol}^{-1} = \Delta H^0{}_f(\mathbf{11}_{HF}) - \Delta H^0{}_f(\mathbf{10}_{HF}) \tag{11b}$$

In order to relate this enthalpy difference to the calculated values and our experiments, we must incorporate an enthalpy of transfer ($\Delta H^0{}_{transf}$) from HF to THF for **10** and **11**, which leads to equation (12).

$$\begin{aligned} \Delta H^0{}_f(\mathbf{11}_{THF}) - \Delta H^0{}_f(\mathbf{10}_{THF}) &= 6{\cdot}1\ \text{kcal mol}^{-1} + \Delta H^0{}_{transf}(\mathbf{11})_{HF\rightarrow THF} \\ &\quad - \Delta H^0{}_{transf}(\mathbf{10})_{HF\rightarrow THF} \end{aligned} \tag{12}$$

Mackor *et al.*[17] determined $\Delta H^0{}_{transf}(\mathbf{10})_{HF\rightarrow heptane}$ = −4·3kcal mol^{-1}. From literature data [27] it can be derived that enthalpies of solution for neutral alkylbenzenes (in cyclohexane, benzene, MeOH, acetonitril, DMSO) are 1 kcal mol^{-1} or less for most solvents. Therefore we may write

$$\Delta H^0{}_{transf}(\mathbf{10})_{HF\rightarrow heptane} \approx \Delta H^0{}_{transf}(\mathbf{10})_{HF\rightarrow THF} \tag{13}$$

To estimate the enthalpy of transfer for **11** from HF to THF, the Born–Bjerrum equation[28] is applied (equation (14)).

$$\Delta H^0{}_{transf,g\rightarrow s} = -e^2 N(1 - 1/\varepsilon - T(\partial\varepsilon/\partial T)/\varepsilon^2)/2R \tag{14}$$

in which $\Delta H^0_{\text{transf,g}\rightarrow\text{s}}$ is the enthalpy difference between an ion with radius R in the gas phase and dissolved in a solent (S) with a dielectric constant ε; N is Avogadro's number. The difference of ΔH^0_{THF} and ΔH^0_{HF} equals $\Delta H^0_{\text{transf}}$ of the calculated ion. With an estimated $R = 2{\cdot}5$ Å for **11** we obtain for HF at $-20\,°\text{C}$ ($\varepsilon = 111$, $\partial\varepsilon/\partial T = -1{\cdot}19$),[29] $\Delta H^0(\mathbf{11})_{\text{g}\rightarrow\text{HF}} = -67{\cdot}5\,\text{kcal mol}^{-1}$ and for THF ($\varepsilon = 9{\cdot}00$, $\partial\varepsilon/\partial T = -4{\cdot}2 \times 10^{-2}$),[30] $\Delta H^0(\mathbf{11})_{\text{g}\rightarrow\text{THF}} = -67{\cdot}8\,\text{kcal mol}^{-1}$ leading to $\Delta H^0_{\text{transf}}(\mathbf{11})_{\text{HF}\rightarrow\text{THF}} = -0{\cdot}3\,\text{kcal mol}^{-1}$.

In view of the uncertainties involved in the calculations with equation (14), the enthalpy of transfer from HF to THF is virtually zero. This result is due to the terms $1/\varepsilon$ and $T(\partial\varepsilon/\partial T)/\varepsilon^2$ in equation (14) which are mutually compensating. Liquid HF is highly structured by formation of molecular chains. As a result its dielectric constant is high. Increase in temperature breaks down the molecular chains, leading to a rather high and negative temperature coefficient of the dielectric constant. On the contrary there is hardly any structure formation in liquid THF. Its (low) dielectric constant is determined by the dipole moment and the polarizibility of the molecules only, and consequently $\partial\varepsilon/\partial T$ is low and negative.

Introducing the two $\Delta H^0_{\text{transf}}$ into equation (12) yields equation (12a)

$$\Delta H^0_{\text{f}}(\mathbf{11}_{\text{THF}}) - \Delta H^0_{\text{f}}(\mathbf{10}_{\text{THF}}) = 10{\cdot}1\,\text{kcal mol}^{-1} \tag{12a}$$

As indicated in equation (7), $\Delta H^0_{\text{f}}(\mathbf{10}_{\text{THF}})$ can be calculated from $\Delta H^0_{\text{f}}(\mathbf{10}_{\text{calc}})$, the theoretical value for the gaseous **10**, by equation (15). As ΔH^0_{s} is usually smaller than 1 kcal mol^{-1},[27] it is omitted because the error thus introduced is much smaller than the uncertainty associated with the theoretical calculations; $\Delta H^0_{\text{v}} = 9{\cdot}8\,\text{kcal mol}^{-1}$.[29]

$$\Delta H^0_{\text{f}}(\mathbf{10}_{\text{THF}}) = \Delta H^0_{\text{f}}(\mathbf{10}_{\text{calc}}) - \Delta H^0_{\text{v}} + \Delta H^0_{\text{s}} = \Delta H^0_{\text{f}}(\mathbf{10}_{\text{calc}}) - 9{\cdot}8 \tag{15}$$

Combining equations (15) and (12) we can calculate $\Delta H^0_{\text{f}}(\mathbf{11}_{\text{THF}})$ ($5{\cdot}9\,\text{kcal mol}^{-1}$ and $16{\cdot}5\,\text{kcal mol}^{-1}$ for MNDO and MINDO/3, respectively). From these values for $\Delta H^0_{\text{f}}(\mathbf{11}_{\text{THF}})$ we obtain $\Delta H^0_{\text{transf}}$ via equation (16)

$$\Delta H^0_{\text{f}}(\mathbf{11}_{\text{THF}}) = \Delta H^0_{\text{f}}(\mathbf{11}_{\text{calc}}) + \Delta H^0_{\text{transf}} \tag{16}$$

which leads to $\Delta H^0_{\text{transf}} = -188{\cdot}5\,\text{kcal mol}^{-1}$ for MNDO and $\Delta H^0_{\text{transf}} = -173{\cdot}3\,\text{kcal mol}^{-1}$ for MINDO/3.

According to Taft[31] the relative stabilities of delocalized positive ions in the gas phase and in aqueous solution are the same. This strongly suggests a low solvent dependence, and we may therefore apply the $\Delta H^0_{\text{transf}}$ values to all calculated benzenonium ions.

The calculated gas phase data of the neutral compounds have to be combined with ΔH^0_{v} and ΔH^0_{s} according to equation (15). From the known values of ΔH^0_{v} for **5a**, **10**, **12** and **14**,[29] it can be concluded that an average ΔH^0_{v} of 11 kcal mol^{-1} is a reasonable estimate. The final values for all calculated species are given in Table 1.

In order to evaluate the enthalpies of reaction ($\Delta H^0_{\text{r,THF}}$) of the protonation reaction in THF described in this work, we have to consider the following equation.

$$\Delta H^0_{\text{f}}(\text{BH}^+_{\text{THF}}) - \Delta H^0_{\text{f}}(\text{B}_{\text{THF}}) - \Delta H^0_{\text{f}}(\text{H}^+_{\text{THF}}) = \Delta H^0_{\text{r,THF}} \tag{17}$$

The $\Delta G^0_{\text{transf}}(\text{H}^+)$ from H_2O to THF is 0 kcal mol^{-1}.[32] From literature data[33] it can be seen that the entropy contribution $-T\Delta S^0_{\text{transf}}$ in $\Delta G^0_{\text{transf}}(\text{H}^+)$ from H_2O to other organic solvents is smaller than $0{\cdot}5\,\text{kcal mol}^{-1}$. We may therefore use $\Delta G^0_{\text{transf}}(\text{H}^+) \simeq \Delta H^0_{\text{transf}}(\text{H}^+)$ as an approximation in equation (17). Since $\Delta H^0_{\text{f}}(\text{H}^+)$ in H_2O equals zero by definition,[26] the $\Delta H^0_{\text{r,THF}}$ is given by equation (18); these values are referred to in the discussion.

$$\Delta H^0_{\text{r,THF}} = \Delta H^0_{\text{f}}(\text{BH}^+_{\text{THF}}) - \Delta H^0_{\text{f}}(\text{B}_{\text{THF}}) \tag{18}$$

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