Fluorination Effect on the Structural Properties of Selected Benzocyclopropenes

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Structures and electronic aspects of mono- and poly-annelated benzocyclopropenes and their gem-disubstituted fluorine derivatives are examined theoretically at the HF/6-31G* and MP2/6-31G* levels of theory. The computed geometries of benzocyclopropene and gem-difluorinated benzocyclopropene are in good qualitative agreement with experimental information. It appears that geminal difluorination leads to a reversed or anti-Mills–Nixon (MN) distortion of the aromatic nucleus (*i.e.* lengthening of the adjacent or *ortho* bonds), in contrast to the pure hydrocarbon systems, where a regular MN bond fixation pattern occurs. The tris-annelated perfluorobenzocyclopropene shows the most pronounced anti-MN effect with *ortho* bonds 0.022 Å longer than in free benzene. This finding is of interest since anti-MN systems are more the exception than the rule. The origin of the MN and anti-MN distortions are interpreted in terms of rehybridization, partial π-electron localization, hyperconjugative interaction with the CF_2-groups and intramolecular charge transfer caused by electronegativity differences. Energetic consequences of fusion of small rings are briefly discussed employing homodesmic reactions.

Structures and properties of fused molecules involving an aromatic nucleus and small rings have attracted considerable attention among organic chemists since these systems embody an interplay of two very important empirical principles: aromaticity and angular strain. The stabilizing and destabilizing interactions are intermingled in fused compounds, often resulting in unusual features.[1–5] Small, highly strained rings significantly distort the aromatic part of the molecule, thus affecting its structure and aromatic stability and consequently its chemical reactivity. It was observed by Mills and Nixon,[6] as early as 1930, that the α and β positions in the benzene fragment exhibit different reactivity toward electrophilic substitution reactions in indane and tetralin, respectively. This finding was rationalized by assuming that fusion of the five-membered ring in indane leads to partial π-electron localization due to ring strain, whilst the same does not occur with the larger, six-membered ring as in tetralin. Even though the original experiments turned out later to be questionable, the Mills–Nixon (MN) hypothesis has since then been considered and disputed by a number of researchers resulting in an interesting and stimulating controversy. The Mills–Nixon effect can be measured by several criteria: the bond distance variation within the benzene moiety being the most direct and simplest probe for its detection, although not applicable to systems with very small fused rings (see below). Experimental evidence provided by X-ray diffraction techniques is ambiguous. In some cases alternations of C–C bond lengths (the so-called bond fixation) are observed[7–12] whereas in others conclusive evidence is seemingly lacking.[13,14] The latter conclusion was recently supported by NMR experiments, which were interpreted solely in terms of π-bond orders,[15–17] thus implying that the MN effect depends exclusively on the pairing scheme of the π-electrons. Since fusion of small rings causes a substantial rehybridization at the carbon junction atoms, the situation is certainly more complex and calls for closer scrutiny. Modern methods of computational quantum chemistry are particularly useful in this respect since they are capable of giving valuable information about structural properties of medium size molecules.[18] The first theoretical paper on the MN effect in indane and tetralin was published almost 60 years ago by Sutton and Pauling.[19] Using a simple valence-bond (VB) approach coupled with the concept of σ-strain described by empirical CC stretching force constants they showed that a distortion in indane was indeed in accordance with the original hypothesis of Mills and Nixon. Subsequent early theoretical treatments by Longuet-Higgins and Coulson were based on π-electron methods and have led to wrong conclusions.[20] The failure of π-electron methods is not surprising since angularly strained rings possess properties which in most cases are mainly governed by the σ-frame. Later, all-valence electron semi-empirical calculations[21,22] were in agreement with the MN postulate as were simple *ab initio* calculations.[23] In contrast, other *ab initio* quantum chemical investigations concluded that the concept of bond fixation was of no use in understanding either the geometry or the chemistry of benzocyclopropene.[24,25] Despite the fact that the MN type of bond fixation was confirmed in recent *ab initio* calculations in model systems of a deformed benzene where the C–H bonds were bent to angles smaller than 120°,[26–28] it was concluded that in real molecules the angular strain is to a large extent relieved by formation of bent 'banana bonds', leading to negligible MN effects even in benzo-cyclobutene and cyclopropene.[27] Obviously, a systematic theoretical study employing methods as reliable as possible is desirable to shed more light on this controversially discussed topic. Our previous theoretical investigations are reviewed elsewhere.[28] Briefly, it appears that the MN effect is operative in fused systems involving three- and four-membered rings,[29–32] which can be easily deduced if suitable reference systems are chosen. On the other hand, it is rather small or even negligible in benzenes with annelated five- or six-membered carbocycles.[34] Further, we could show that the extent of the MN-effect can be modulated through a judicious choice of substituents placed at particular positions in the molecule.[32] In specific cases this can lead to a cancellation or even an anti-MN type of distortion.[35] Clearly, the results of annelation of small rings to a benzene moiety depends strongly on their size, their number and relative positions (*ortho-*, *meta-*) as well as the nature of substituents and their sites in the corresponding derivatives. Hence, no quick generalizations are possible implying that each family of

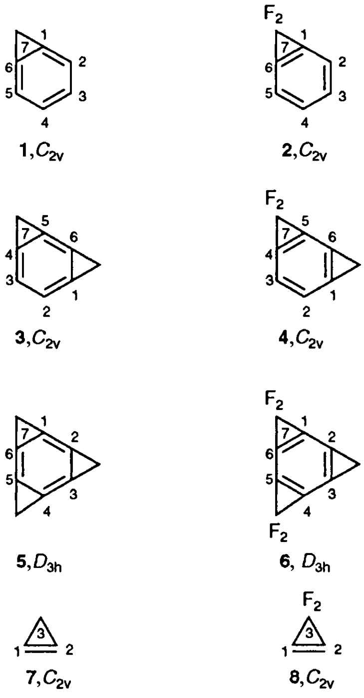

Fig. 1

annelated molecules should be studied separately. In this paper we examine the influence of fluorination on the structural and energetic features of mono- and poly-annelated benzocyclopropenes depicted in Fig. 1. Since multiple fluorination often leads to unexpected results,[36] its influence on the MN effect is of great interest.

Methodology

Standard *ab initio* molecular orbital calculations have been performed using GAUSSIAN 86[37] and GAUSSIAN 92[38] computer programs. To establish the appropriate theoretical level we optimized the geometries of the molecules for which experimental data are available (**1**, **2**, benzene and cyclopropene) at the Hartree–Fock (HF) level and with inclusion of valence-electron correlation through Møller–Plesset perturbation theory terminated at second order (MP2). Several one particle basis sets of increasing flexibility were employed. Besides the usual series of basis sets of increasing size, we also added the 6-31 + G* basis set, which is augmented by additional diffuse sp-functions. Such functions are often required to properly describe situations with many electron lone pairs, such as in the fluorinated species **2**, **4** and **6**. As shown in Table 1, compound **2**, benzene and cyclopropene exhibit the expected behaviour: bond lengths are underestimated at the HF level, whilst the MP2 equilibrium geometries are in good to very good agreement with the experimental numbers. RMS errors in the bond distances between 0.001 and 0.003 Å are in the expected range for the MP2/6-31G* method. It is also apparent that the addition of diffuse functions is not mandatory for the description of **2** since the only parameter which is significantly changed upon addition of such functions is the C–F bond length, which is not of particular importance in the current investigation. The situation is completely different and somewhat unusual for **1**. HF/6-31G* reproduces the experimental geometry fairly well with an RMS error in the bond lengths of 0.003 Å and a maximum deviation of 0.013 Å. The d,p-polarized and the triple-valence 6-311G* basis sets offer an only marginal, if any, improvement over 6-31G*. Unexpectedly, the inclusion of electron correlation now leads to a dramatic deterioration of the agreement between calculated and measured numbers. The RMS error triples to 0.008–0.009 Å and at MP2/6-311G* the maximum error is as high as 0.025 Å with a systematic overestimation of the bond lengths within the benzene rings by 0.020–0.025 Å. It is hard to understand why MP2/6-31G* (and similar basis sets), which otherwise are known to provide good theoretical predictions for equilibrium geometries[18] is so much in error for **1**. Even though this question cannot be settled at this point, here we will base our discussion on the fully optimized (within the given point group symmetry) MP2/6-31G* structures. It should, however, be kept in mind that while this level will certainly reproduce qualitative trends well, since the latter involves relative changes between similar bonds estimated within the same model, its quantitative predictions should be taken with due caution. For a general description of the theoretical models and their performance, the reader is referred to the excellent discussion in ref. 18.

Results and Discussion

Structures.—The MP2/6-31G* and HF/6-31G* optimized minimum energy structures for compounds **1**–**6**, cyclopropene (**7**) and 3,3-difluorocyclopropene (**8**) are displayed in Tables 1 and 2, the corresponding total energies can be found in Table 5. As pointed out earlier, a proper choice of reference molecules is crucial for understanding the MN-effect.[28,32] The ipso C(1)–C(6) bond† is highly strained due to the presence of the three-membered ring and its properties are somewhere in between those of a double bond found in such a free three-membered ring and a normal benzene CC bond. Thus, this bond length will be compared here to the mean of the benzene bond length and the double bond distance in cyclopropene (calc., 1.350; exp., 1.346 Å; Table 1). Although a choice of the arithmetic mean of these two bond lengths as a reference is somewhat arbitrary, it is certainly better than a use of the benzene CC distance. The remaining carbon–carbon bond lengths of the aromatic nucleus are less problematic and can be compared with the free benzene value (calc., 1.397, exp., 1.395 Å). The changes in bond lengths of molecules **1**–**6** upon annelation in this scheme are summarized in Table 3. Using the computed data, the ipso bond length in **1** is slightly shorter than the reference value whereas the *ortho* bond is compressed by 0.015 Å. Further, the *meta* and *para* bond lengths are 0.012 and 0.011 Å longer than in free benzene, respectively (Tables 2 and 3). Performing the same analysis using the experimental instead of the computed geometries for **1**, benzene, and cyclopropene leads to similar results. The shortening of the ipso and *ortho* bonds in the X-ray structure of **1** is more pronounced, being 0.012 and 0.032 Å, respectively. Also the *meta* and *para* bonds are slightly shorter than in benzene, in contrast to the theoretical results, where these bonds are slightly longer. These small changes in **1** and the small numerical inconsistencies between calculations and experiments indicate that the underlying effects are subtle and not easy to reproduce. Nevertheless, the qualitative key result is the same with both data sets: The *ortho* bond is substantially shortened, indicating a Mills-Nixon kind of bond localization in **1**. Fluorination of the methylene group in **1** leading to **2** has a large effect on the geometry as seen from the data in Table 2. As expected, the largest influence is exerted on the C(1)–C(7) bond, which is theoretically predicted to be shortened by 0.045 Å. This is in good accordance with the experimental estimate of 0.050 Å. More importantly, small but significant changes are induced within the benzene ring upon fluorination. It appears that the bond fixation scheme is changed as evidenced by the data

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† The bonds in the annelated aromatic systems will be labelled as ipso (annelated bonds), *ortho* (adjacent bonds) and *meta* and *para*. In **3** and **4**, where two different types of adjacent bonds are present, it will be explicitly stated to which bond we will refer.

Table 1 Computed and experimental structural parameters of **1**, **2**, benzene and **7**; distances in Å, angles in degrees

Molecule	Bond/Angle	HF/ 3–21G	HF/ 6–31G*	HF/ 6–31G**	HF/ 6–311G*	MP2/ 6-31G*	MP2/ 6–311G*	MP2/ 6–31 + G*	exp.
1	C(1)–C(2)	1.362	1.370	1.370	1.370	1.382	1.385	1.384	1.363(3)[a]
	C(2)–C(3)	1.406	1.400	1.400	1.400	1.409	1.412	1.412	1.387(4)
	C(3)–C(4)	1.390	1.395	1.395	1.394	1.408	1.410	1.410	1.390(5)
	C(1)–C(6)	1.337	1.332	1.332	1.332	1.352	1.356	1.353	1.334(4)
	C(1)–C(7)	1.517	1.494	1.494	1.496	1.503	1.508	1.507	1.498(3)
	C(7)–H	1.076	1.081	1.081	1.080	1.092	1.090	1.092	—
	C(2)–H	1.070	1.075	1.075	1.075	1.088	1.087	1.088	0.94(3)
	C(3)–H	1.072	1.076	1.076	1.076	1.088	1.088	1.089	0.93(3)
	RMS error[b,c]	0.005	0.003	0.003	0.003	0.008	0.009	0.009	
	C(1)–C(6)–C(7)	63.8	63.5	63.6	63.6	63.3	63.3	63.3	63.6
	C(1)–C(6)–C(5)	124.7	124.7	124.7	124.6	124.6	124.5	124.6	124.5(2)
	C(1)–C(2)–C(3)	113.1	113.0	113.0	113.2	113.0	113.1	113.0	113.2(2)
	C(2)–C(3)–C(4)	122.1	122.3	122.3	122.2	122.5	122.4	122.4	122.4(4)
	H–C(7)–H 115.2	113.1	113.0	113.0	113.2	113.2	113.9	113.6	—
	H–C(5)–C(4)	121.7	121.6	121.6	121.5	121.7	121.6	121.6	122(2)
	H–C(4)–C(3)	118.7	118.5	118.5	118.5	118.4	118.4	118.4	121(2)
	RMS error[b]	0.10	0.08	0.08	0.06	0.08	0.08	0.09	
2	C(1)–C(2)	1.375	1.390	1.390	1.390	1.392	1.394	1.394	1.389[d]
	C(2)–C(3)	1.388	1.379	1.379	1.378	1.398	1.401	1.400	1.387
	C(3)–C(4)	1.407	1.416	1.415	1.416	1.417	1.418	1.420	1.415
	C(1)–C(6)	1.343	1.337	1.336	1.335	1.372	1.377	1.374	1.360
	C(1)–C(7)	1.462	1.449	1.449	1.448	1.458	1.461	1.453	1.448
	C(7)–F	1.359	1.333	1.333	1.329	1.363	1.352	1.374	1.357–1.369
	C(2)–H	1.069	1.073	1.074	1.073	1.087	1.086	1.087	—
	C(3)–H	1.072	1.076	1.076	1.075	1.087	1.087	1.088	—
	RMS error[b]	0.005	0.006	0.006	0.006	0.003	0.004	0.005	
	C(1)–C(6)–C(7)	62.7	62.6	62.5	62.5	61.9	61.9	61.8	
	C(1)–C(6)–C(5)	124.5	124.4	124.4	124.4	124.1	124.0	124.2	
	C(1)–C(2)–C(3)	112.9	112.8	112.8	112.9	113.1	113.2	112.9	
	C(2)–C(3)–C(4)	122.6	122.8	122.8	122.7	122.8	122.8	122.9	
	F–C(7)–F	106.1	106.4	106.4	106.4	106.6	107.0	106.0	
	H–C(5)–C(4)	122.3	122.3	122.2	122.2	122.1	122.0	122.2	
	H–C(4)–C(3)	118.1	117.9	117.9	117.9	118.1	118.1	118.0	
Benzene	C–C	1.385	1.386	1.386	1.388	1.397	1.399	1.399	1.395
	C–H	1.072	1.076	1.076	1.076	1.087	1.087	1.088	1.087
7	C(1)–C(2)	1.282	1.279	1.276	1.275	1.303	1.305	1.305	1.296
	C(1)–C(3)	1.523	1.494	1.495	1.498	1.507	1.514	1.511	1.509
	C(1)–H	1.058	1.068	1.067	1.067	1.079	1.078	1.079	1.072
	C(3)–H	1.075	1.083	1.083	1.082	1.091	1.090	1.091	1.088
	RMS error[b]	0.007	0.006	0.006	0.006	0.003	0.003	0.003	
	C(1)–C(2)–C(3)	65.1	64.7	64.7	64.8	64.4	64.5	64.4	64.6
	H–C(3)–H	115.0	112.9	113.0	113.2	113.5	114.2	113.9	114.6
	H–C(1)–C(2)	149.6	150.2	150.1	149.9	149.9	149.8	149.9	149.9
	RMS error	0.30	0.58	0.54	0.47	0.37	0.14	0.24	

[a] R. Neidlein, D. Christen, V. Poignee, R. Boese, D. Bläser, A. Gieren, C. Ruiz-Perez and T. Hübner, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 295. [b] RMS error $= \frac{1}{n}[\Sigma_i(P_i - P_i^0)^2]^{\frac{1}{2}}$. P. R. Taylor, in *Lecture Notes in Quantum Chemistry*, ed. B. O. Roos, Springer Verlag, Berlin, 1992. [c] C–H bond lengths excluded. [d] R. Boese, personal communication. We thank Professor Boese for providing these results prior to publication.

presented in Table 3. The ipso, *ortho* and *para* bonds are now elongated relative to the bond distances in **1** whilst the *meta* bond is shorter. The experimental X-ray data of **1** and **2** (Tables 1 and 2) show the same qualitative picture with one notable exception. The *para* and *ortho* bonds are lengthened upon fluorination by 0.025 and 0.026 Å, respectively, but somewhat surprisingly, the *meta* bonds remain virtually unchanged. As in the case for **1**, there are small discrepancies between theory and experiment when the changes in the bond lengths with respect to the reference distances are considered (Table 3). Despite these slight imperfections and peculiar lengthening of the ipso bond, both computational and experimental data agree that in **2** the bond pattern is now more consistent with a reversed or anti-MN-effect, as indicated in particular by the longer *ortho* bond.

Bis- and tris-fusion in systems **3**–**6**, for which no experimental data are available, follow the same pattern, but to a considerably larger extent. Thus, in **3** the MN-bond fixation is more pronounced as evidenced by a shorter *ortho* C(5)–C(6) and a much longer *meta* C(2)–C(3) distance, compared to the corresponding distances in **1**, respectively. Also the ipso bonds are elongated. The fluorinated counterpart, **4**, offers the opposite type of bond fixation as expected. The ipso bonds are less lengthened than in the transition from **1** to **2**. In contrast, the *ortho* bonds are more elongated than earlier in harmony with the anti-MN localization scheme. In the highly substituted and D_{3h} symmetric systems **5** and **6** the MN and anti-MN distortions are considerably more pronounced. In **5**, the ipso bond is increased to 1.379 Å and the *ortho* bonds have become

Table 2 Structural parameters computed at MP2/6-31G* (HF/6-31G* data in parentheses) of **3**–**8**; distances in Å, angles in degrees

Bonds/Angle	**3**	**4**	**5**	**6**	**7**	**8**
C(1)–C(2)	1.389 (1.375)	1.407 (1.413)	1.369 (1.355)	1.397 (1.408)	1.301 (1.279)	1.327 (1.299)
C(2)–C(3)	1.424 (1.416)	1.402 (1.376)	1.379 (1.359)	1.381 (1.332)	1.505 (1.494)	1.445 (1.435)
C(1)–C(7)	1.512 (1.493)	1.468 (1.451)	1.508 (1.497)	1.471 (1.456)		
C(5)–C(6)	1.373 (1.360)	1.392 (1.395)				
C(1)–C(6)	1.361 (1.341)	1.372 (1.332)				
C(7)–H/F	1.092 (1.081)	1.357 (1.327)	1.092 (1.080)	1.352 (1.323)	1.091 (1.083)	1.368 (1.342)
C(2)–H	1.088 (1.075)	1.087 (1.073)			1.078 (1.068)	1.080 (1.069)
C(1)–C(6)–C(7)	63.5 (63.3)	62.2 (62.9)	62.8 (63.0)	62.0 (62.8)		
C(1)–C(2)–C(3)	116.1 (115.9)	116.2 (115.9)	120.0 (120.0)	120.0 (120.0)	64.4 (64.7)	62.6 (63.1)
C(2)–C(1)–C(6)	125.9 (126.2)	126.5 (126.9)				
C(1)–C(6)–C(5)	117.9 (117.9)	117.9 (117.2)				
C(6)–C(1)–C(7)	62.8 (63.1)	61.9 (62.5)				
H/F–C(7)[a]–H/F	113.1 (113.1)	107.2 (106.8)	113.2 (113.2)	107.9 (107.3)	113.5 (112.9)	106.0 (105.9)
H–C(2)–C(3)	119.1 (120.1)	120.7 (121.2)				
H–C(1)–C(2)					150.0 (150.2)	148.0 (148.9)

[a] For **7** and **8**: H/F–C(3)–H/F.

Table 3 Changes in bond lengths of **1**–**6** with respect to the mean of benzene and the double bond in cyclopropene (ipso bond) and the benzene bond distance (remaining bonds) computed at MP2/6-31G*, HF/6-31G* (in italics) and from experimental data (in parentheses); data in Å

Bond	**1**	**2**	**3**	**4**	**5**	**6**
ipso	−0.002 *−0.001* (−0.012)	+0.022 *+0.004* (+0.014)	+0.011 *+0.008*	+0.023 *−0.001*	+0.019 *+0.026*	+0.031 *−0.001*
ortho	−0.015 *−0.016* (−0.032)	−0.005 *+0.004* (−0.006)	−0.024,[a] −0.008[b] *−0.026,[a] −0.011[b]*	−0.005,[a] +0.010[b] *−0.009,[a] +0.027[b]*	−0.018 *−0.031*	−0.000 *−0.022*
meta	+0.012 *+0.014* (−0.008)	+0.002 *−0.007* (−0.008)	+0.027 *+0.030*	+0.005 *−0.010*		
para	+0.011 *+0.009* (−0.005)	+0.020 *+0.030* (+0.020)				

benzene: 1.397, *1.386*, (1.395)
½ [benzene + cyclopropene]: 1.350, *1.333* (1.346)

[a] C(5)–C(6) bond. [b] C(1)–C(2) and C(3)–C(4) bonds.

shorter still, being 0.028 Å shorter than in free benzene. As a consequence, the difference between the *ortho* and ipso bond distances becomes very small. On the contrary, anti-MN distortion takes place in **6**, the difference between the two types of bond lengths being 0.016 Å. The *ortho* bond in **6** is equal to that in free benzene implying that the rehybridization effect is completely cancelled out by the π-electron redistribution (*vide infra*). It follows that the fluorination blows up the benzene fragment by stretching the ipso- and *ortho*-bonds, the effect being more pronounced in the latter. The same conclusion can be drawn when the bond length variation with respect to the reference distances in Table 3 are analysed. As a final comment one should point out that the HF/6-31G* method seems to exaggerate both MN and anti-MN deformations. The qualitative inferences are however the same.

Interpretation.—Numerical values discussed so far are interesting in their own right, but a deeper understanding and interpretation is provided by simple and qualitative models such as rehybridization, π-electron (de)localization, hyperconjugation and intramolecular charge transfer. It is well established that the carbon junction atoms undergo significant rehybridization, shifting s-character from ipso to *ortho* bonds.[28–33] This is corroborated by the data displayed in Table 4. The s-character of the local hybrid orbitals are extracted from the first order density matrix computed with the semiempirical MNDO[39] scheme calculated both at the HF/6-31G* and MP2/6-31G* optimized geometries, following the approach introduced by Trindle and Sinanoglu.[40] Our experience is that hybridization indices obtained by the MNDO wavefunctions are rather close to the classical hybridization model introduced by Pauling.[41] The data in Table 4 show that for all compounds considerable deviations from the standard sp^2 hybridization in benzene are present. The ipso bonds are described by approximately sp^3–sp^3 hybridization, while the *ortho* bonds exhibit hybridizations with increased s-content. The differences in hybridization between the pure hydrocarbons (**1**, **3**, **5**) and the fluorinated systems (**2**, **4**, **6**) in these bonds are only minor. However, fluorine substitution induces a dramatic rehybridization at the carbon atom C(7). The s-character is decreased in the C–F bonds whereas hybrid orbitals within the three-membered ring originating from C(7) have an unusually high s-content of some 29% as compared with ≈ 18% s-character in pure hydrocarbons. This result is in accord with the Walsh–Bent rule which states that electronegative atoms prefer bonding to atoms possessing hybrid orbitals with high p-content (and *vice versa*).[42] It is

Table 4 Character and π-bond orders as computed by MNDO wavefunctions employing optimized MP2/6-31G* and HF/6-31G* geometries. The latter results are given within parentheses. For numbering see Fig. 1.

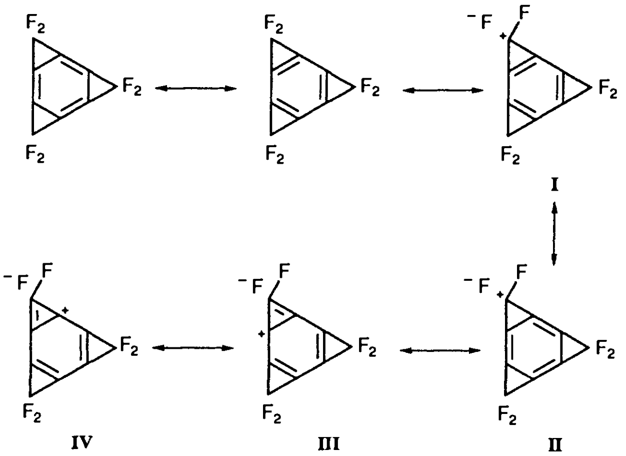
		s-Characters		π-Bond orders	
Molecule	Bond	$CX_2 \equiv CH_2$	$CX_2 \equiv CF_2$	$CX_2 \equiv CH_2$	$CX_2 \equiv CF_2$
	C(1)–C(2)	42.0–31.9 (41.9–32.1)	42.2–31.2 (41.5–31.0)	0.67 (0.67) [0.69][a]	0.65 (0.61)
1 ($CX_2 \equiv CH_2$)	C(2)–C(3)	32.8–33.1 (32.8–33.1)	33.3–33.3 (33.6–33.7)	0.66 (0.65) [0.64]	0.68 (0.72)
	C(3)–C(4)	33.1–33.1 (33.2–33.2)	32.7–32.7 (32.4–32.4)	0.68 (0.67) [0.69]	0.65 (0.61)
2 ($CX_2 \equiv CF_2$)	C(1)–C(6)	25.1–25.1 (25.7–25.7)	24.4–24.4 (25.8–25.8)	0.64 (0.65) [0.63]	0.66 (0.69)
	C(1)–C(7)	30.9–18.7 (30.6–18.7)	31.2–29.6 (30.7–29.4)	0.13 (0.13) [0.09]	0.16 (0.16)
	C(7)–H(F)	31.0 (31.0)	23.3–13.7 (23.5–14.9)		
3 ($CX_2 \equiv CH_2$)	C(1)–C(2)	42.0–32.3 (41.9–32.4)	41.8–31.2 (40.8–30.7)	0.69 (0.68) [0.70]	0.63 (0.57)
	C(2)–C(3)	32.9–32.9 (32.9–32.9)	33.6–33.6 (34.2–34.2)	0.64 (0.64) [0.61]	0.69 (0.75)
4 ($CX_2 \equiv CF_2$)	C(1)–C(6)	25.2–24.6 (25.1–25.8)	25.3–24.6 (26.1–27.0)	0.63 (0.64) [0.60]	0.68 (0.74)
	C(1)–C(7)	30.8–18.7 (32.8–18.6)	30.7–29.7 (32.9–29.0)	0.13 (0.13) [0.08]	0.15 (0.15)
	C(5)–C(6)	40.9–40.9 (40.8–40.8)	40.5–40.5 (39.6–39.6)	0.68 (0.67) [0.72]	0.63 (0.56)
	C(7)–H(F)	31.1 (31.0)	23.3–13.7 (24.2–15.2)		
5 ($CX_2 \equiv CH_2$)	C(1)–C(2)	41.1–41.1 (41.1 –41.1)	40.3–40.3 (39.2–39.2)	0.78 (0.70) [0.74]	0.63 (0.54)
	C(2)–C(3)	24.2–24.2 (25.0–25.0)	25.3–25.3 (27.1–27.1)	0.50 (0.61) [0.57]	0.68 (0.76)
6 ($CX_2 \equiv CF_2$)	C(1)–C(7)	33.4–18.6 (32.7–18.7)	32.9–29.3 (32.2–29.2)	0.13 (0.13) [0.07]	0.15 (0.15)
	C(7)–H(F)	30.9 (31.1)	23.6–13.7 (23.8–14.8)		
7 ($CX_2 \equiv CH_2$)	C(1)–C(2)	31.3–31.3 (32.8–32.8)	31.4–31.4 (32.3–32.3)	0.99 (0.99)	0.97 (0.98)
	C(1)–C(3)	23.5–17.9 (23.0–19.0)	24.2–29.6 (23.9–29.4)	0.13 (0.13)	0.18 (0.18)
8 ($CX_2 \equiv CF_2$)	C(3)–H(F)	30.8 (30.8)	23.1–13.6 (23.4–14.7)		
	C(1)–H	42.8 (40.8)	41.3 (40.9)		

[a] π-Bond orders within brackets are obtained from model HMO calculations (see text).

noteworthy that the hybridization indices calculated for HF/6-31G* and MP2/6-31G* geometries are very similar implying that they are highly insensitive to small variations in structural parameters. This feature enables their transferability for similar molecular fragments in various large molecules.[45]

The fusion of cyclopropene ring(s) to benzene leads to MN-type of bond alternation due to rehybridization at the carbon junction atoms as described above in **1**, **3** and **5**. π-Electron localization is not highly pronounced but follows the rehybridization picture (Table 4). The data in Table 4 show that also the formal single C(1)–C(7) bonds have π-bond orders of 0.13 for the hydrocarbons and 0.15–0.16 for the fluorinated systems. This is most likely due to hyperconjugative interaction of the pseudo CX_2-π* orbitals (X = H or F) with the benzene π-system. To substantiate this interpretation we have performed model HMO calculations on the hydrocarbon systems where the CH_2-group is replaced by a doubly occupied pseudo π-AO, in analogy with the treatment of CH_3-groups.[43] The pseudo π-AO of methylene is then considered as a heteroatom Y with the following relevant integrals: $\alpha_Y = \alpha_0 + h_Y\beta_0$ and $\beta_{CY} = k_{CY}\beta_0$, with $h_{CH_2} = 2$ and $k_{CCH_2} = 0.7$ adopted from ref. 43. The resulting π-bond orders are compared with those estimated fom the MNDO calculations employing the HF/6-31G* and MP2/6-31G* geometries. The degree of similarity is remarkable (Table 4). We stress that both rehybridization and (hyper)conjugation act in a concerted way in the parent hydrocarbons leading to the partial π-bond localization.

Even though the hybridization pattern of the ring carbon atoms in the fluorinated systems (**2**, **4**, **6**) is very similar to that found in the parent hydrocarbons, π-electron density of the benzene ring is shifted towards the ipso bonds (Table 4), leading to a reversed MN-type of bond fixation. How can this seemingly counterintuitive behaviour be understood? A possible explanation is based on the electrostatic argument that the π-electron charge drift is caused by the highly positively charged gem-disubstituted carbon atoms. Thus, an efficient shielding of the positive partial charges is achieved. This hypothesis is consistent with the high polarizability of the benzene nucleus and with the reorganization effect found in ESCA chemical shifts where inner-core positive holes are almost completely shielded by the electron redistribution during the photoionization process.[44] The difference in hyperconjugative interaction of the pseudo CX_2-π* orbitals (X = H or F) with the benzene π-system offers an additional argument. Due to the high electronegativity of fluorine, the pseudo π* orbitals are much lower in energy for the CF_2 groups than the corresponding CH_2 orbitals. Consequently, stabilizing hyperconjugation will be more pronounced in the fluorinated compounds, as already indicated by the higher π-bond orders of the C(1)–C(7) bond in the fluorinated systems. Unfortunately, HMO parameters for CF_2-groups are not available. Hence, we have to resort to the VB structures depicted in Schemes 1 and 2. A simple counting of the VB structures shows that localization of the π-electron density on the ipso bond is expected. Furthermore, VB structure **I** will certainly have more weight than **II** since the formally aromatic cyclopropenyl cation arrangement emerges. In the hydrocarbon case, the VB structures **I**–**IV** will be of much less importance, while structures **V**–**VIII** will not appear at all. We conclude that in the fluorinated compounds the shift of π-electron density towards the ipso bonds caused by hyperconjugation is in

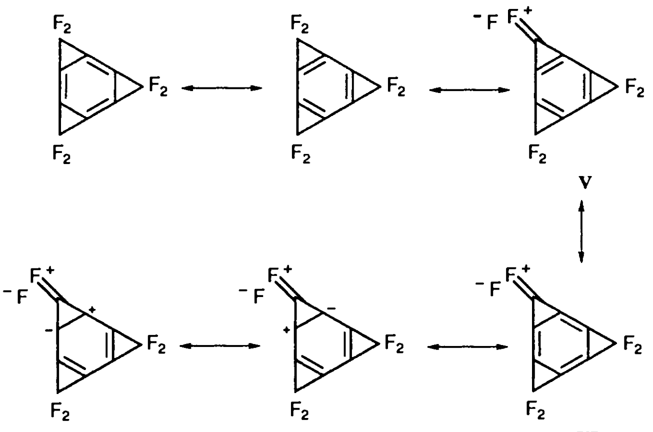


IV III II

Scheme 1

Table 5 Total energies (hartree) computed at HF/6–31G* and MP2/6–31G*

Molecule	HF/6-31G*	MP2/6–31G*
1	−268.463 11	−269.353 57
2	−466.178 27	−467.403 85
3	−306.215 93	−307.242 20
4	−701.644 51	−703.33995
5	−343.968 59	−345.132 55
6	−937.106 11	−939.272 66
7	−115.823 05	−116.205 25
8	−313.544 94	−314.260 92
Benzene	−230.703 14	−231.457 73
Ethane	− 79.228 76	−79.494 74
Propane	−118.263 62	−118.660 31
(*E*)-but-2-ene	−156.110 41	−156.625 92
o-xylene	−308.770 64	−309.793 84

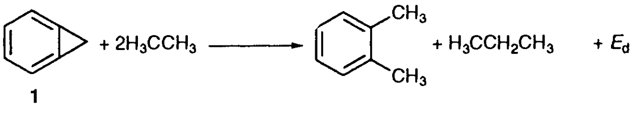


Scheme 2

harmony with electronic shielding of the positive peripheral carbon atoms but counteracts the rehybridization picture. The former two effects apparently prevail.

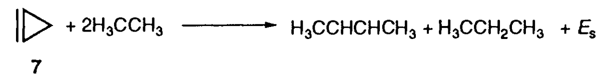
Lengthening of the C(1)–C(7) bond in **6** relative to 3,3-difluorocyclopropene is interesting and perhaps unexpected. Let us consider the changes upon fusion in two steps. Assume that the C(1)–C(7) bond in **6** is frozen at the 3,3-difluorocyclopropene value whereas the ipso bond distance takes its final value of 1.381 Å. The C(1)–C(7)–C(6) angle becomes 57.0°. In the second step C(1)–C(7) is relaxed to its optimal distance of 1.471 Å. This leads to a decrease in the C(1)–C(7)–C(6) angle to 56.0°. The change is small but surprising since the smaller bond angle increases the angular strain. Further, the hybrid AO placed at C(1) and directed towards C(7) has a substantially higher s-character than in 3,3-difluorocyclopropene (32.9% and 24.2%, respectively). High s-character generally implies a shorter bond and yet the contrary takes place. Apparently, there must be a new feature here. This is indeed the case: the electronegativity of a hybrid orbital depends on its s-character and two hybrids forming a covalent bond between atoms of similar electronegativity tend to assume s-contents which are as close as possible.[45] However, C(7) bears a high positive partial charge leading to a much higher electronegativity than expected from the hybrid's composition. According to the Walsh–Bent rule[42] the C(7) atom requires a higher p-character of the hybrid placed at C(1), but rehybridization acts in the opposite direction—it transmits s-character into the C(1)–C(7) bond. Or, in other words, the χ_{17} hybrid with its high s-content tries to withdraw electron density from the electron deficient C(7) carbon, which is of course unfavourable. We conclude that higher s-content is not necessarily advantageous for an optimal bonding in this particular case and that in the perfluoro compound **6**, it actually leads to a longer C(1)–C(7) bond.

Energies and Stabilities.—Fusion of small rings to aromatic fragments leads to considerable destabilization of the resulting system. The reason for this destabilization is twofold: (i) annelation causes additional angular deformation; and (ii) partial π-electron localization perturbs the aromatic system.† The best way to estimate destabilization energies is provided by hypothetical homodesmic reactions in which the number of structural groups and specific types of covalent bonds (classified according to the hybridization of the atoms) is kept constant.[47,48] Thus, effects due to zero point energies, correlation energy, basis set deficiency, *etc*, are expected to largely cancel. The destabilization energy in benzocyclopropene can be estimated by the reaction shown in Scheme 3.



Scheme 3

Using the computed energies from Table 5 a destabilization energy E_d of 71.3 kcal mol^{-1} is obtained (experimentally this number amounts to 68 kcal mol^{-1}).[2] Interestingly, the destabilization energy for **1** is higher than that computed for cyclopropene, **7**, from the homodesmic reaction (Scheme 4). E_s can be



Scheme 4

attributed to angular strain and amounts to 57.4 kcal mol^{-1}, which compares well with the strain energy of 54.5 kcal mol^{-1} obtained by the group increment approach. This increase in strain is easily understood in terms of rehybridization following the bending of the H–C═C bond angle in cyclopropene (150.2°) to the C(2)–C(1)–C(6) angle of 124.7° in **1**. Additional destabilization is due to the slight π-electron localization as evidenced by a variation in π-bond orders (Table 4).

The three homodesmic reactions [eqns. (1)–(3)] allow an insight into the degree of destabilization caused by fluorination.

$$\mathbf{2} + 1\cdot[\mathbf{7}] \longrightarrow \mathbf{1} + 1\cdot[\mathbf{8}] + E_{\text{dest}} \quad (1)$$

$$\mathbf{4} + 2\cdot[\mathbf{7}] \longrightarrow \mathbf{3} + 2\cdot[\mathbf{8}] + E_{\text{dest}} \quad (2)$$

$$\mathbf{6} + 3\cdot[\mathbf{7}] \longrightarrow \mathbf{5} + 3\cdot[\mathbf{8}] + E_{\text{dest}} \quad (3)$$

The destabilization energy $E_{\text{dest}}^{(k)}$ is expected to increase with the number of CF_2 groups for the reasons discussed above. The perturbation of the aromatic π-sextet is larger in the fluorinated systems **2**, **4** and **6** than in the corresponding hydrocarbons **1**, **3** and **5** and its magnitude increases with increasing number of CF_2 groups. Further, the π-electron localization in the fluorinated systems is opposite to that in the unsubstituted molecules and counteracts with the local σ-orbitals. Since σ- and π-electrons do not act in a concerted way, a less favourable electron distribution arises. Finally, hybrids with increased s-character emanating from the benzene carbons towards CF_2 groups are not advantageous (see above). The computed destabilization energies of $E_{\text{dest}}^{(k)}$ of 3.4, 8.5 and 16.9 kcal mol^{-1} for $k = 1, 2, 3$, respectively, support the reasoning. It is,

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† The latter point is only valid if the classical interpretation for the stability of aromatic compounds as originating from the delocalized π-system is valid. For a different point of view see ref. 46.

however, difficult to trace back the various contributions to the destabilization energy and there is certainly more work required to satisfactorily elucidate this question.

Conclusions

Convincing evidence is provided by quantum chemical *ab initio* calculations at the HF/6-31G* and MP2/6-31G* level that the geminal difluorination of benzocyclopropenes leads to reversed or anti-Mills–Nixon type of distortion of the benzene fragment. The magnitude of the deformation depends on the number of fused three-membered rings. In mono-annelated systems angular deformations (shape) of the benzene ring are highly pronounced, but the changes in bond distances (size) are rather small. The opposite is the case in tris-annelated perfluorobenzocyclopropene. Here, the bond angles are ideal (120°), since they are determined by symmetry, but the bond distances exhibit significant variation around the ring perimeter. The origin of the anti-MN-effect is found in the large polarizability of the benzene nucleus and the 'mobility' of the π-electrons. They are shifted to the ipso bond(s) for two reasons: (i) in order to efficiently shield the high positive partial charge at the fluorine substituted carbon atom(s); and (ii) to increase the hyperconjugative interaction between the benzene moiety and the CF_2 groups. Thus, cyclopropenyl cation-like aromatic peripheral fragments are formed, which are apparently energetically favourable. The possibly important role of hyperconjugation in pure hydrocarbons involving four-membered rings was recently discussed by Streitwieser, Vollhardt *et al.*[49] These authors believe that hyperconjugation is a dominant effect in the perturbation of the benzene ring. Recent EPR measurements, however, re-emphasize the non-negligible influence of rehybridization.[50] Finally, the destabilization of benzocyclopropene with respect to cyclopropene and benzene and the destabilizing effect of difluorination is discussed by means of homodesmic reactions. As expected, the largest destabilization is found in tris-annelated perfluorobenzocyclopropene and can be traced to the antagonistic behaviour of rehybridization and hyperconjugation. The latter is further enhanced by the electrostatic shielding effect of the positively charged disubstituted carbon atoms leading to a partial π-bond localization in the ipso bonds.

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