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Push−Pull vs Captodative Aromaticity

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Vinylogs of fulvalenes with cyclopropenyl and cyclopentadienyl moieties attached either to different carbon atoms (c-C_3H_2−CH=CH−C_5H_4-c, **7**) or to the same carbon atom [X=C(c-C_3H_2)(c-C_5H_4), **10**] [X = CH_2; $C(CN)_2$; $C(NH_2)_2$; $C(OCH_2)_2$; O; c-C_3H_2; c-C_5H_4; SiH_2; CCl_2] of the double bond inserted between the two rings are examined theoretically at the B3LYP/6−311G(d,p) level. Both types of compounds are shown to possess aromaticity, which was called "push−pull" and "captodative" aromaticity, respectively. For the captodative mesoionic structures X=C(c-C_3H_2)(c-C_5H_4), the presence of both the two aromatic moieties and the C=C double bond is the necessary and sufficient condition for their existence as energetic minima on the potential energy surface. Aromatic stabilization energy (ASE) was assessed by the use of homodesmotic reactions and heats of hydrogenation. Spatial magnetic criteria (through space NMR shieldings, TSNMRS) of the two types of vinylogous fulvalenes **7** and **10** have been calculated by the GIAO perturbation method employing the nucleus independent chemical shift (NICS) concept of Paul von Ragué Schleyer, and visualized as iso-chemical-shielding surfaces (ICSS) of various sizes and directions. TSNMRS values can be successfully employed to visualize and quantify the partial push−pull and captodative aromaticity of both the three- and five-membered ring moieties. In addition, the push−pull effect in compounds **7** and **10** could be quantified by the occupation quotient $\pi^*_{C=C}/\pi_{C=C}$ of the double bond inserted between the two rings.

1. Introduction

Aromaticity has always been one of the most intriguing concepts in organic chemistry (for reviews, see refs 1 and 2). With time, it was modified by including the molecules with heteroatoms, three-dimensional and charged systems (see, e.g., refs 2−5 and references cited therein). Hückel's $4n + 2$ rule defines the number of π-electrons forming the ring current required for the system to be aromatic. Therefore, some unsaturated cyclic hydrocarbons with an odd number of carbon atoms must eliminate either a proton or a hydride anion to form charged aromatic moieties. Cyclopentadienyl anion and cyclopropenylium or tropylium cations are the most popular examples.

In a previous paper,[6] the aromaticity of fulvalenes was investigated as quantified and visualized by the through space NMR shielding (TSNMRS) cones of the fulvalene moieties within the framework of the previously elaborated approach.[7,8] Fulvalenes are molecules with two unsaturated ring systems showing cross conjugation through the interring double bond and capable of generating two separate aromatic moieties. They can be considered a result of dehydrogenation of their precursors with the saturated C−C interring bond as shown in Scheme 1 on the example of dehydrogenation of 5-(2-cyclopropenyl)-1,3-cyclopentadiene **1** leading to 5-(2-cyclopropenyliden)-1,3-cyclopentadiene **2** (calicene).

SCHEME 1

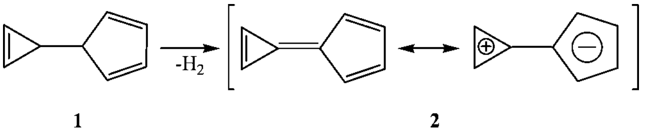
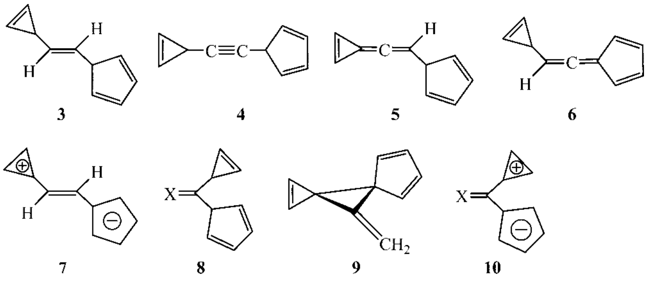


CHART 1[a]



[a] X = CH_2 (a); $C(CN)_2$ (b); $C(NH_2)_2$ (c); $C(OCH_2)_2$ (d); O (e); SiH_2 (f); c-C_2H_2 (g); c-C_5H_4 (h); CCl_2 (i).

The goal of the present study was to analyze the vinylogs of calicene **2**, which are compounds in which the two aromatic moieties, separated by a C=C double bond, may be attached either to different carbon atoms of the C=C bond or to the same carbon atom to give the vicinal or geminal isomers, respectively, in order to answer the question whether such systems are aromatic and, if so, to compare the relative aromaticity of the three- and five-membered ring moieties with that of calicene. For this reason, the following molecules as well as some related structures (cf. Chart 1) were calculated theoretically and analyzed with respect to their aromaticity and partial aromaticity of the two ring moieties. Therefore, TSNMRS were calculated and employed to visualize and quantify the spatial magnetic properties of **7** and **10**. In addition, the occupation quotient

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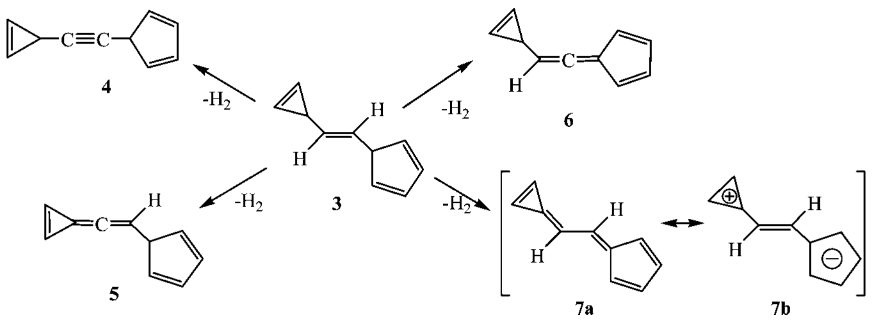
SCHEME 2



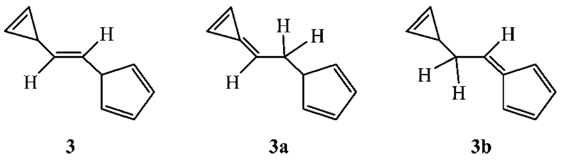
$\pi^*_{C=C}/\pi_{C=C}$ of the double bond in **7** and **10** was applied to quantify the push–pull effect in the latter compounds.

2. Computational Methods and Calculations. The geometry optimization and energy calculations were performed at the B3LYP/6–311G(d,p) level of theory without restrictions using the *Gaussian 03* suite of programs.[9] The effect of the solvent polarity was approximated using the integral equation formalism for the polarizable continuum model (IEF-PCM).[10] The chemical shieldings surrounding the molecules were calculated on the basis of the NICS concept[11] whereby the molecule was placed in the center of a grid of ghost atoms ranging from −10.0 to +10.0 Å in all three dimensions with a step width of 0.5 Å resulting in a cube of 68 921 ghost atoms. The chemical shielding calculations were performed using the GIAO[12] method at the same B3LYP/6–311G(d,p) level of theory. From the GIAO calculations, the coordinates and isotropic shielding values of the ghost atoms were extracted. After transformation of the tabulated chemical shieldings into the SYBYL[13] contour file, the TSNMRSs were visualized as ICSSs, providing a 3D view of spatial extension, sign, and scope of the aromaticity/ring current effects at each point in the space. The occupations of the bonding and antibonding orbitals of the calicene vinylogs (**7** and **10**) interring C=C double bonds ($\pi^*_{C=C}/\pi_{C=C}$) were calculated using the NBO option[14] as implemented in the *Gaussian 03* package.

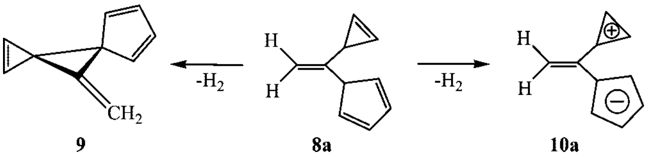
3. Results and Discussion

3.1. Push–pull vs Captodative Aromaticity Subjected to Heats of Hydrogenation. Dehydrogenation of 5-[(*E*)-2-(2-cyclopropenyl)ethenyl]-1,3-cyclopentadiene **3**, which can be considered a vicinal vinylog of the calicene precursor **1**, may follow several alternative routes. For example, 2,3-dehydrogenation of compound **3** gives the acetylenic compound 5-[2-(2-cyclopropenyl)ethynyl]-1,3-cyclopentadiene **4**; the 1,2- and 3,4-dehydrogenations result in cumulenes 5-[2-(2-cyclopropenyliden)vinyl]-1,3-cyclopentadiene **5** and 5-[2-(2-cyclopropenyl)ethenylidene]-1,3-cyclopentadiene **6**, respectively, whereas 1,4-dehydrogenation leads to 5-[2-(2-cyclopropenyliden)ethylidene]-1,3-cyclopentadiene **7**, which may be represented as a combination of the two resonance structures, **7a** and **7b** (cf. Scheme 2).

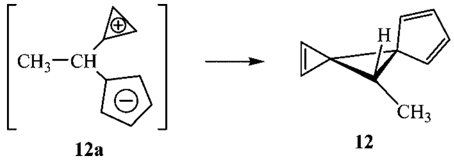
CHART 2



SCHEME 3



SCHEME 4



Among the isomeric molecules **4**–**7**, compound **7** is the most stable structure, apparently, due to partial aromaticity generated owing to the contribution from structure **7b**. The acetylenic compound **4** is 28.3 kcal/mol less stable, and the cumulenes **5** and **6** are less stable by 31.3 and 16.2 kcal/mol, respectively. Therefore, compound **7** can be considered a representative of push–pull alkenes and the aromaticity represented by structure **7b** can be called push–pull aromaticity. The high dipole moment of **7** (5.93 D), by far exceeding that of its precursor **3** (0.74 D), confirms a notable contribution of the resonance structure **7b**. An independent indication of the push–pull aromaticity of compound **7** is provided by analysis of its geometry. Contribution from structure **7b** should lengthen the exocyclic double bonds (1.347 and 1.364 Å, respectively) and shorten the formally single central bond (1.431 Å) with respect to the 1,3-butadiene derivative **7a** (1.337 Å and 1.456 Å, respectively).

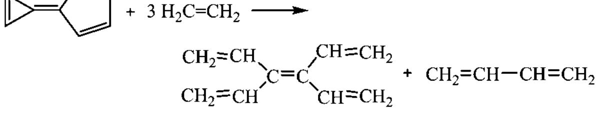
It is interesting to mention that compound **3** is not the most stable structure as far as the position of the double bond in the interring chain is concerned; calculations show it to be 3.5 kcal/mol more stable than its isomer **3a** but 7.0 kcal/mol less stable than its isomer **3b**. Therefore, the presence of a cyclopentadienylidene moiety stabilizes molecules **6** and **3b** as compared to their isomers with the cyclopropenylidene moiety **5** and **3a** (cf. Chart 2), apparently due to the more extended system of π-conjugation in **3b** (three conjugated π-bonds) than in **3** or **3a** (only two conjugated π-bonds).

Another interesting and, to the best of our knowledge, hitherto unknown type of aromaticity appears if the geminal isomers of the vinylogs of fulvalenes are considered, that is, compounds with the two aromatic moieties attached to the same carbon atom of the C=C double bond. The simplest compound of this type, the geminal vinylog of calicene, **10a**, could be obtained by 1,3-dehydrogenation of 5-[1-(2-cyclopropenyl)vinyl]-1,3-cyclopentadiene **8a** without formation of a C–C bond directly connecting the two rings, as shown in Scheme 3:

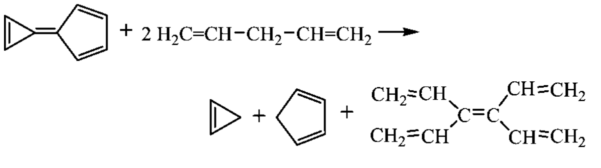
Besides the mesoionic compound **10a**, possessing two aromatic fragments, the dehydrogenation of compound **8a** may afford also 9-methylenedispiro[2.0.4.1]nona-1,5,7-triene **9**. The principal question is whether structure **10a** corresponds to a minimum on the potential energy surface or its optimization would result in direct binding of the two rings leading to spirocycle **9**. The calculations showed that **10a** is an independent structure, fully planar (unlike molecule **9**), with the distance between the substituted carbon atoms of the two rings by far exceeding that of molecule **9** (2.420 Å and 1.560 Å, respectively), which corresponds to a real minimum on the potential energy surface since all eigenvalues of the Hessian matrix are positive. Structure **10a** is isomeric to structure **7b** and is an overall neutral but internally charged mesoionic molecule. Therefore, we face in **10a** a new type of aromaticity which we call captodative aromaticity, by analogy with captodative olefins, that are olefins, geminally substituted with both an acceptor and a donor.[15−17]

Molecule **10a** must be less aromatic than **7**, since the two aromatic fragments in **10a** are not directly conjugated. Indeed, dehydrogenation of **8a** to **10a** in Scheme 3 is less favorable by 2.95 kcal/mol than its dehydrogenation to the dispirocycle **9**. However, the mesoionic compound **10a** has a much larger dipole moment (8.48 D) than the dispirocycle **9** (2.12 D) so that one might expect that in polar solvents this energy difference may be leveled out or even inverted. That is just what is happening in solution as calculated by the polarized continuum model IEF-PCM. Even in the chloroform solution, the mesoionic compound **10a** becomes more stable than the dispirocycle **9** by 2.82 kcal/mol, and in the DMSO solution, this energy difference increases to 5.25 kcal/mol in favor of **10a**.

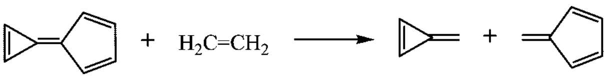
To assess and compare the aromatic stabilization energies (ASE) for calicene **2** and its push−pull **7** and captodative **10a** vinylogs, the energies of the corresponding homodesmotic reactions[18] were calculated, similar to the approach used by Scott et al.[19] and Cyrañski et al.[20] For each molecule, three types of homodesmotic reactions were considered: (i) reactions of the reference compounds with ethylene to afford 1,3-butadiene and the completely opened structures [reactions 1, 4, and 7]; (ii) reactions with 1,4-pentadiene to afford cycloalkenes and tetrakis(vinyl)ethylene [reactions 2, 5, and 8]; (iii) reactions with ethylene to afford fulvenes [reactions 3, 6, and 9]. The problem with evaluation of ASE for mesoionic molecules like **10a** is that it is practically impossible to find proper reference compounds for a homodesmotic reaction to simulate a hypovalent state of the *ipso*-carbon atoms in the charged aromatic rings. Therefore, the energies of the homodesmotic reactions 7−9 should be considered as having only an illustrative character.



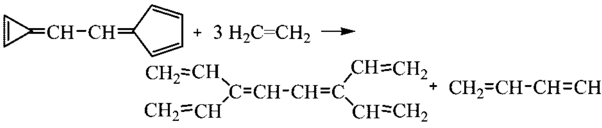
(1)



(2)



(3)



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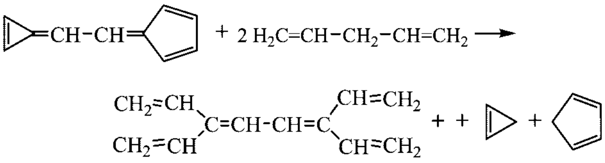

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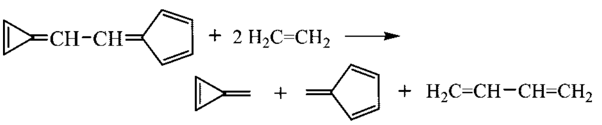
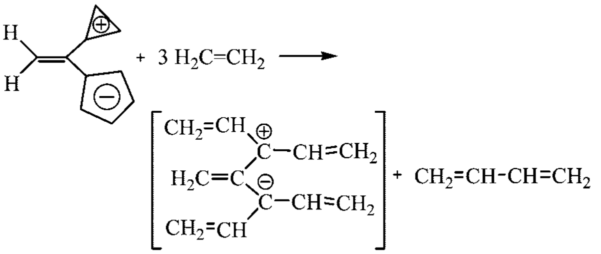
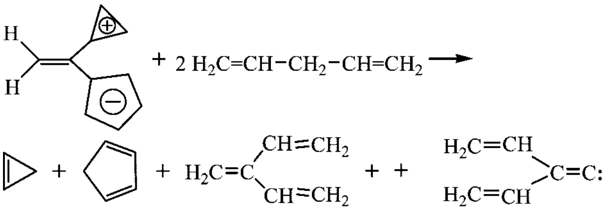


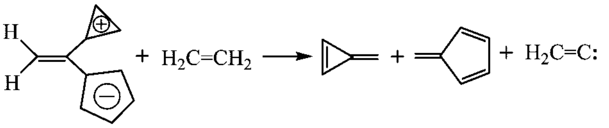
(6)



(7)

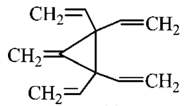


(8)



(9)

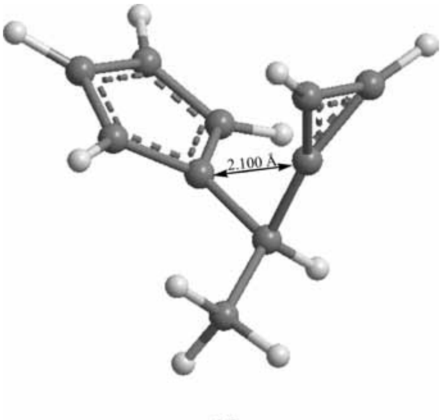
Noteworthy, whereas structure **10a** lacking a covalent bond between the two rings corresponds to a real minimum on the potential energy surface and is clearly distinct from the isomeric dispiro structure **9**, a similar open structure in square brackets in reaction 7 does not correspond to a minimum but rather is optimized into 3-methylene-1,1,2,2-tetravinylcyclopropane **11** with the C_{sp^3}−C_{sp^3} bond (1.627 Å) being not much longer than that in 9-methylenedispiro[2.0.4.1]nona-1,5,7-triene **9** (1.560 Å).



11

This means that it is the aromatic character of the two rings in molecule **10a** that makes this highly polar structure a minimum on the potential energy surface. This hint should be considered an independent indication of specific captodative aromaticity also of other compounds **10** (vide infra). Another reason for molecule **10a** to be a stable minimum on the potential energy surface could be the presence of the C=C double bond in the molecule that allows the two aromatic moieties to be conjugated through the C_{sp^2} carbon atom. To verify or disprove this hypothesis, we have calculated the mesoionic structure **12a** (cf. Scheme 4), which is a saturated analogue of **10a**, isomeric to 5-[1-(2-cyclopropenyl)vinyl]-1,3-cyclopentadiene **8a**. It turned out that structure **12a** does not correspond to a minimum on the potential energy surface and during the geometry optimization is transformed into 9-methyldispiro[2.0.4.1]nona-1,5,7-triene **12**. The C—C bond connecting the two spiro carbon atoms in **12** is even shorter than that in **9** (1.530 vs 1.560 Å). This means that the presence of the C═C double bond in molecules **10** is a necessary condition (and, in conjunction with the presence of the two geminal aromatic fragments, also the sufficient condition) for these structures to be minima on the corresponding potential energy surfaces. The energy of compound **12** is 9.2 kcal/mol higher than that of its isomer **8a** due to steric strain caused by cyclization.

Since the mesoionic structure **12a** is highly polar (the dipole moment for the starting nonoptimized geometry is ~10 D as compared to 2.0 D for the final optimized structure **12**), we have examined whether it would be stabilized in solution. The results of calculations performed by the use of the polarized continuum model were drastically different for a low polar (chloroform) and a polar (DMSO) solvent. In low polar chloroform (ε 4.7), structure **12a** is optimized into dispirocycle **12**, as it is in the gas phase. The length of the C−C bond between the two spiro carbon atoms after optimization corresponds to a normal value (1.539 Å) close to that in the gas phase (1.530 Å). The dipole moment is low (2.69 D), and no substantial charge separation takes place. On the contrary, in highly polar DMSO (ε 49), the optimized structure **13** retains the original mesoionic character with large dipole moment of 9.64 D and is found to be a clearly distinct local minimum lying 4.4 kcal/mol higher than its spirocyclic isomer **12** (also calculated in DMSO solution).



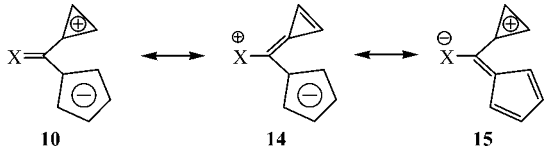
13

No conjugation between the two aromatic moieties separated by the methine carbon atom is possible, and the two rings in **13** turn about the MeCH-C_{sp^2} bonds by ~90° to minimize the repulsion. With this, the positive charge is localized on the cyclopropenyl fragment (+0.504 e) and the negative charge on the cyclopentadienyl fragment (−0.585 e). The distance between the substituted carbon atoms of the two aromatic moieties (2.100 Å) substantially exceeds the length of an ordinary C−C bond. Therefore, the conclusion can be made that, in spite of the absence of conjugation between the two rings, the geminal mesoionic aromatic structure **13** can be stabilized in highly polar media. Note that, whereas the fully planar molecule **10a** with the two rings geminally conjugated through the C_{sp^2} atom is a minimum on the potential energy surface even in the gas phase, it becomes more stable than its dispirocyclic isomer **9** already in low polar chloroform; the less aromatic structure **13** becomes a minimum only in highly polar DMSO.

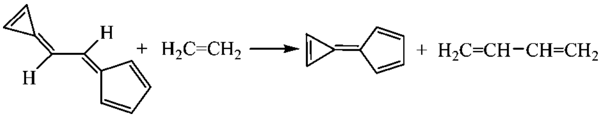
TABLE 1: B3LYP/6-311G(d,p) Calculated Energies for Homodesmotic Reactions 1−10 (ΔE, kcal mol^{-1})

reaction	ΔE
(1)	−57.3
(2)	4.6
(3)	5.9
(4)	−61.7
(5)	0.2
(6)	4.5
(7)	−64.6
(8)	54.1
(9)	53.4
(10)	−1.4

SCHEME 5



The energies ΔE of the homodesmotic reactions 1−9 are given in Table 1. The first type of homodesmotic reactions [reactions 1, 4, and 7] gives unreasonably large negative ΔE values, apparently, due to ring strain increasing the energy of the reactants and being absent in the products. Homodesmotic reactions 1 and 5 give small positive ASE values, since the positive contribution from aromaticity of compounds **2** and **7** is nearly counterbalanced by the presence of exocyclic double bond(s) in the reactants. Finally, reactions 8 and 9 have enormously large ASE values, apparently because of the aforementioned reasons concerning the specific character of mesoionic molecules. Therefore, to assess captodative aromaticity of **10a**, it seems more reasonable to compare its total energy with the energy of its isomer **7**. In turn, the push−pull aromaticity of **7** with respect to aromaticity of calicene **2** is most properly reproduced by the homodesmotic reaction 10. Its energy is as low as −1.4 kcal/mol (Table 1), i.e., the ASE values for molecules **2** and **7** are quite comparable. Following this logic, the captodative aromaticity of **10a** can be evaluated to be 38 kcal/mol less than that of its vicinal isomer **7**.



(10)

In order to analyze how the relative push−pull (as represented by structure **7b**) versus captodative (as represented by structure **10a**) aromaticity depends on the nature of group X in compounds **10**, a series of mesoionic structures **10a−h** as well as their dihydrogenated precursors **8a−h** with different X (Chart 1) were calculated. The effect of X should reflect the relative contribution of the resonance structures **14** and **15** given in Scheme 5.

The optimized geometries and the charge distribution in molecules **7** and **10a−h** are shown in Figure 1, and their heats of hydrogenation (including that of calicene **2**, as a reference compound) are given in Table 2.

Although the total energy of **7** with respect to **10a** is 38.5 kcal/mol lower, the larger charge transfer in **10a** (Figure 1) might be indicative of its greater aromaticity. This apparent inconsistency can be explained as follows: the larger stability (which, in terms of ASE, is identical to aromaticity) of **7** is because of

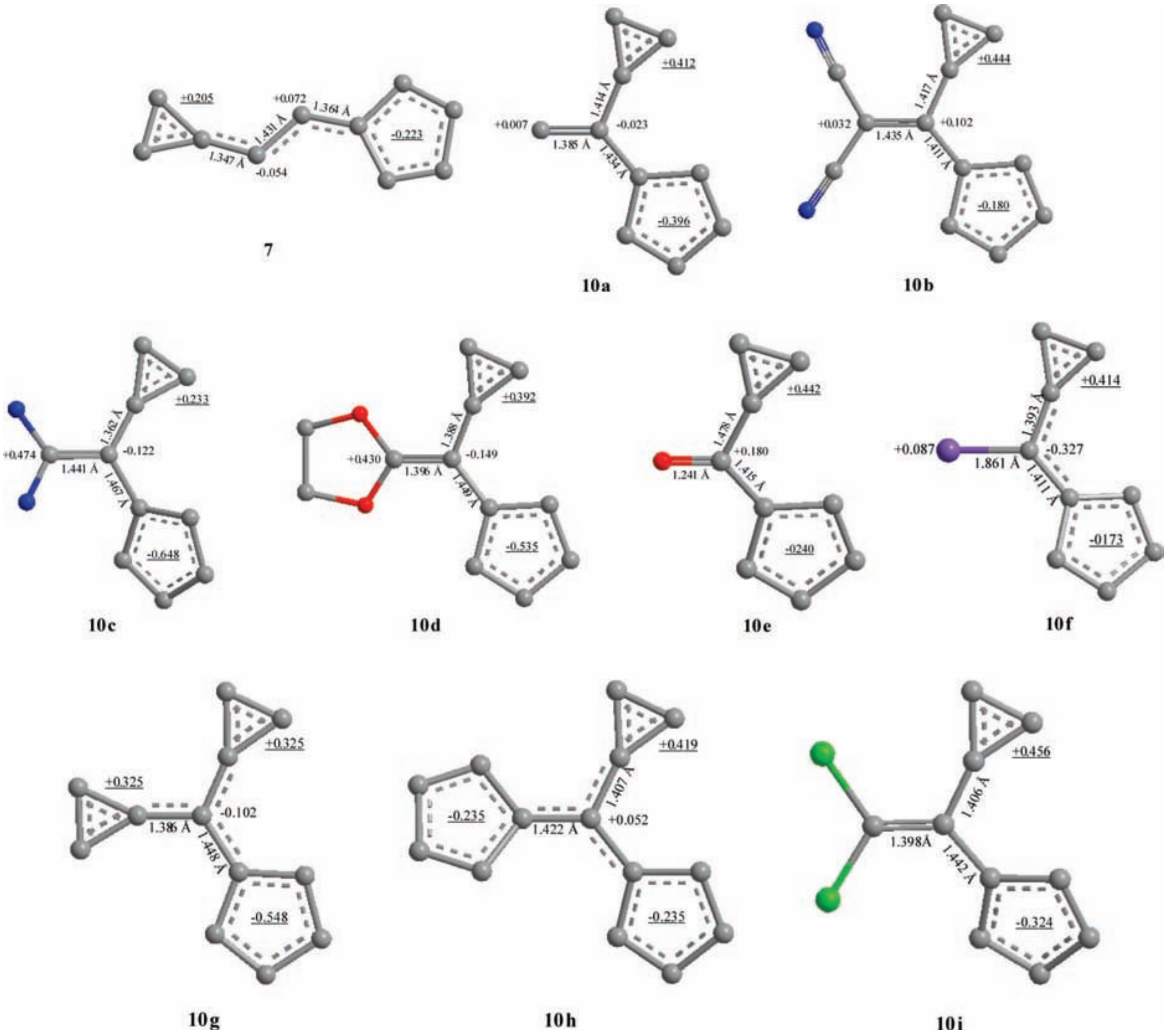


Figure 1. Optimized geometries and charge distribution in molecules **7** and **10a**−**i**.

TABLE 2: Heats of Hydrogenation (ΔE, kcal mol^{-1})

reagent	product	X	$-\Delta E$ [a]
2	**1**	-	19.6
7	**3**	-	16.8
10a	**8a**	CH_2	54.8
10b	**8b**	$C(CN)_2$	40.5
10c	**8c**	$C(NH_2)_2$	35.2
10d	**8d**	$C(OCH_2)_2$	55.4
10e	**8e**	O	52.5
10f	**8f**	SiH_2	32.9
10g	**8g**	*c*-C_3H_2	45.8
10h	**8h**	*c*-C_5H_4	41.9
10i	**8i**	CCl_2	53.5

[a] The heat of hydrogenation of benzene to cyclohexane calculated to one C═C bond is 20.2 kcal mol^{-1}.

its more extended π-system, whereas the smaller charge separation in **7** than in **10a** is due to the fact that the aromatic resonance structure **7b** makes an important but not predominant contribution as compared to that of the major noncharged resonance structure **7a**. On the contrary, for **10a** no resonance structure without a charged ring (either the 3-membered or 5-membered) can be written. Therefore, being less aromatic in general than **7** (in terms of ASE), molecule **10a** has more aromatic 3-membered and 5-membered fragments, in accordance with the NMR criteria (vide infra, section 3.2).

The use of the Julg and Francois[1d] structural criterium of aromaticity *A* reflecting equalization of carbon−carbon bond lengths in molecules **7** and **10a** (and, for comparison, calicene **2**) leads to similar conclusions:

$$A = 1 - \frac{225}{n}\sum\left(1 - \frac{d}{\bar{d}}\right)^2$$

(n is the number of bonds in the ring, d is the bond length, and $\bar{d}$ is the averaged bond length). The values of *A* for the five-membered ring in molecules **2**, **7**, and **10a** are equal to 0.767, 0.719, and 0.918, and for the three-membered ring 0.720, 0.704, and 0.944. This allows one to conclude that aromaticity of the rings as fragments increases in the order **7** < **2** ≪ **10a**; i.e., in the push−pull molecule **7**, it is slightly lower, and in the captodative molecule **10a**, it is substantially higher than in calicene **2**. Therefore, one should differentiate between the aromaticity of the molecule as a whole (assessed from its total energy) and aromaticity of its fragments (assessed on the basis of structural and NMR criteria).

Analysis of the data of Table 2 allows one to conclude that aromaticity of calicene **2** and its vicinal vinylog **7** is very similar, in agreement with very low energy of the homodesmotic reaction 10. Moreover, their aromaticity is very close to that of benzene (see the footnote to Table 2). Judging from the data of Table 2, the geminal analogue of calicene, compound **10a**, is 38 kcal mol^{-1} less aromatic than its vicinal vinylog **7**. As to the question of how strongly this difference is affected by the nature of the terminal group in compounds **10**, it can be seen that variation of substituent X has a considerable effect on the ΔE value varying in the range of 22.5 kcal/mol. Since the contribution of either of the resonance structures **14** and **15** should stabilize the mesoionic structure **10** and, therefore, increase its captodative aromaticity, the exothermicity of hydrogenation of compounds **10b**−**h** is expected to be lowered by either electropositive and electronegative groups X with respect to the unsubstituted compound **10a**. Indeed, the substituents capable of stabilization of either the positive charge (**8c**,**f**,**g**) or the negative charge (**8b**,**h**) on the terminus of the double bond decrease the absolute value of ΔE. The exceptions are compounds **8d**,**e** for which the values of ΔE for hardly understandable reasons are practically the same as for the unsubstituted compound **10a**. The compound with the highest relative captodative aromaticity in this series is the derivative of silaethene **10f**, whose aromaticity is lower by only 12.7 kcal/mol (compare to 34.6 kcal/mol for the parent compound **10a**) than that of benzene.

3.2. Spatial Magnetic Properties of Push−Pull and Captodative Aromatic Compounds 2, 3, 7, and 10. In addition to structural and energetic criteria, of great importance are the magnetic criteria of aromaticity. With this, it is a separate problem: how do all these criteria correlate with each other?[2] Therefore, we have calculated the through space NMR shielding surfaces (TSNMRS) for the calicene vinylogs **7** and **10a**, as well as those of the residual compounds **10** employing the NICS concept of Paul von Rague Schleyer;[21] TSNMRS values can be used to visualize the anisotropic effect of the functional groups and the ring current effect of aromatic moieties by isochemical shielding surfaces (ICSS) of various sizes and signs[7] to thereby quantify the aromaticity and/or antiaromaticity present.[8] This new approach to both quantify and visualize the partial aromaticity of **7** and **10** ring moieties is expected to deliver a comprehensive picture of this topic and to offer a new successful method to be applied for the study of similar phenomena in physical organic chemistry.

The concept of employing spatial NICS[22] for the quantitative analysis of (anti)aromaticity[8,22] was meanwhile extended to solid-state systems[23] and applied to fulvalenes,[6,24] fullerenes,[25] and a large variety of aromatic compounds.[8]

Of significant note, though, there have been some recent developments of NICS[26] showing that none of the various methods can safely assign aromaticity[27] and nonmeasurable parameters have not proven to be generally suitable for quantitative evaluation of aromaticity.[28] For example, NICS analysis was shown to lead to an incorrect prediction of aromaticity for the cyclopropenyl anion.[29]

The TSNMRS values of the isolated cyclopropylidene and pentadienylidene moieties **3a** and **3b** and (for comparison) of tris- (**16**), pentafulvene (**17**), and cyclopropenylium cation (**18**) and benzene (**19**) are visualized as ICSS of different size and sign, and are given in Figure 2; the distances *d*/Å of the ICSS = ±0.1 ppm from the center of the respective ring moiety[8] are collected in Table 3.

In terms of our model,[8] the partial aromaticity of both three- and five-membered ring moieties in the isolated cyclopropylidene and pentadienylidene moieties **3a** and **3b** are higher than in the corresponding fulvenes, studied already.[30] Obviously, these two structures are stabilized via canonical structures **3a′** and **3b′** (cf. Scheme 6) more effectively than the corresponding fulvenes **16** and **17** (Scheme 6, R = H). Next come the push−pull (**7**) and the captodative vinylogs (**10a**) of calicene (**2**): the partial aromaticity of both three- and five-membered ring moieties increases appropriately (see Table 3) but proves to be still smaller (at least for **10a**) than in calicene **2**. The distances at highfield ICSS = +0.1 ppm above/below the center of the three-membered ring moiety in **10a** are somewhat larger

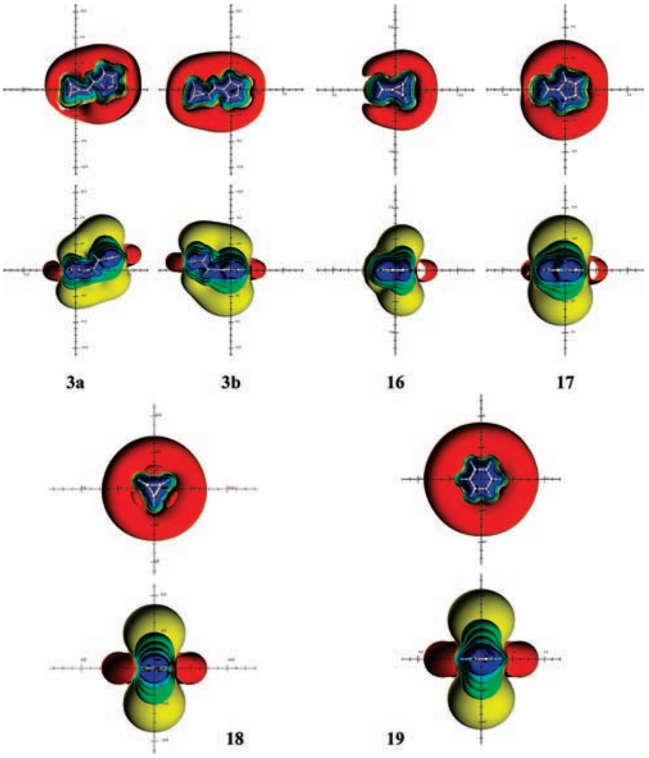


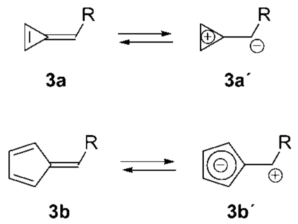
Figure 2. Visualization of the TSNMRSs (ICSSs: blue represents 5 ppm shielding, cyan 2 ppm shielding, green−blue 1 ppm shielding, green 0.5 ppm shielding, yellow 0.1 ppm shielding, and red −0.1 ppm deshielding) of cyclopropylidene and pentadienylidene moieties **3a**,**b**, of tris- and pentafulvenes **16** and **17**, of the cyclopropenylium cation **18**, and of benzene **19**.

TABLE 3: Distances *d*/Å of the ICSS = ±0.1 ppm from the Center of Respected Ring Moieties[8] in 3a,b, 7, 10a, and (for comparison) tris- (16)[30] and pentafulvene (17),[30] calicene 2,[6] the cyclopropenylium cation 18,[30] and benzene 19[30]

	d/Å ICSS = −0.1 ppm (in plane)[a]		*d*/Å ICSS = +0.1 ppm (perpendicular-to-center)[a]	
compound	C_3-ring	C_5-ring	C_3-ring	C_5-ring
3a	4.9	-	6.1	-
3b	-	5.0	-	7.1
7	5.1	5.6	6.5	7.1
10a	5.3	5.5	7.8 (3.9)[c]	7.4 (3.5)[c]
16	4.6	-	5.8	-
17	-	4.9	-	6.2
2	5.2	6.0	7.4 (4.0)[c]	7.9
18	5.9	-	7.2 (4.1)[c]	-
19[b]	-	7.2[b]	-	8.9[b]

[a] For the method, see ref 8. [b] Benzene. [c] Distances *d*/Å at ICSS = ±0.5 ppm.

SCHEME 6



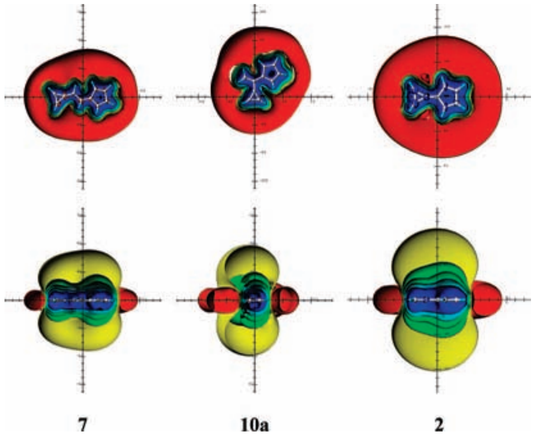


Figure 3. Visualization of the TSNMRSs (ICSSs: blue represents 5 ppm shielding, cyan 2 ppm shielding, green−blue 1 ppm shielding, green 0.5 ppm shielding, yellow 0.1 ppm shielding, and red −0.1 ppm deshielding) of the push−pull (**7**) and the captodative vinylog (**10a**) of calicene **2**.[6]

than in calicene; however, the reason for this is the anisotropic effect of the additional interring C═C double bond. If the distances at ICSS = +0.5 ppm are considered (cf. Table 3), the lower partial aromaticity of the three-membered ring moiety in **10a** than in calicene is readily visible. By comparison of these two vinylogs of calicene, the partial aromaticity of the ring moieties in the captodative vinylog **10a** proves to be higher than in the push−pull vinylog **7** (cf. Table 3); this is in agreement with the different aromaticity of the two compounds (vide supra). However, the higher value of the perpendicular ICSS for **10a** could also be due to a greater cumulative effect of the two rings because they are closer (ca. 4.6 Å) than in **7** (ca. 6.2 Å).

Finally, it can be established that this partial aromaticity of both three- and five-membered ring moieties in **7** and **10a** is not only smaller than in calicene **2**, but the corresponding distances *d*/Å in **2** are smaller than in cyclopropenyl cation **18** and benzene **19** as the two prototypes of 2*π*- and 6*π*-aromaticity, respectively, which is in agreement with the aromaticity of **7** and **10a**, with respect to **2**, **18**, and **19** as well (vide supra).

Thus, in terms of our model,[8] the partial aromaticity values of both the three- and the five-membered ring moieties in both the push−pull (**7**) and the captodative vinylog (**10a**) of calicene **2** are lower than that in the latter compound (all are visualized in Figure 3). Nevertheless, these moieties in all three structures possess partial aromaticity, although it is smaller than in the 2*π*- and 6*π*-aromaticity prototype compounds **18** and **19**. Obviously, direct conjugation in calicene **2** proves to be more effective than via the vinylogous interring C═C double bonds in **7** and **10a** (vide supra).

TABLE 4: Distances *d*/Å of the ICSS = ±0.1 ppm from the Center of the Respected Ring Moieties[a] and Deviation from Planarity in the Captodative Vinylogs 10

	d/Å ICSS = −0.1 ppm		*d*/Å ICSS = +0.1 ppm		
compound	C_3-ring	C_5-ring	C_3-ring	C_5-ring	deviation from planarity
10a	5.3	5.5	7.8	7.4	planar
10b	4.7	5.0	6.9	6.4	planar
10c	5.0	6.0	4.7 (6.5)	8.0	C_3-ring twisted by 2.8° C_5-ring twisted by 50.5°
10d	5.8	6.8	8.3	8.0 (9.0)	C_3-ring twisted by 0.6° C_5-ring twisted by 11°
10e	5.5	5.4	7.7	7.6	planar
10f	5.0	5.0	6.9 (7.0)	6.5 (7.7)	C_3-ring twisted by 9.9° C_5-ring twisted by 27°
10g	6.1	7.0	9.4	9.5	planar
10h	5.4	5.5	8.2	7.3 (8.5)	C_3-ring twisted by 7.8°
10i	4.4	5.3	6.9 (8.0)	7.2(8.5)	C_3-ring twisted by 1.6° C_5-ring twisted by 25.4°

[a] For the method, see ref 8.

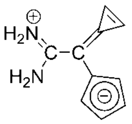
TABLE 5: Bond Lengths bl/Å and Occupation Numbers of the Bonding $\pi_{C=C}$ and Antibonding $\pi^*_{C=C}$ Orbitals of the Interring C═C Double Bond in the Vinylogs 7 and 10 of Calicene 2

compound	substitution	$bl_{=C}$/Å	π^*	π	π^*/π
7	-	1.43	0.545	1.523	0.357
10a	CH_2═	1.38	0.384	1.745	0.220
10b	$(NC)_2C$═	1.44	0.638	1.673	0.381
10i	Cl_2C═	1.40	0.536	1.775	0.302
10d	*c*-$C_3O_2H_4$	1.40	0.433	1.620	0.267
10g	*c*-C_3H_2	1.39	0.405	1.591	0.255
10h	*c*-C_5H_4	1.42	0.510	1.549	0.329
ethylene	-	1.33	0.004	1.995	0.002
1,1-dimethylethylene	-	1.33	0.063	1.966	0.032

Table 4 collects the corresponding data of the captodative vinylogs **10**. In the analogs of **10a**, both the three-membered and five-membered ring moieties are partly aromatic as well. The TSNMRS values visualized as ICSS of various sizes and signs proved the corresponding ring currents to be present. Examining the distances *d*/Å of the ICSS = ±0.1 ppm results in the following general conclusions: (i) Both the reference compound **10a** and the corresponding carbonyl compound **10e** behave similarly; obviously, replacing O═C for CH_2═C is without remarkable influence on the partial aromaticity of the two ring moieties. (ii) This changes if substituents are attached to the terminal position: (−)M substituents [$(NC)_2C$═C; **10b**] reduce the aromaticity of both the three- and five-membered ring moieties, while (iii) (+)M substituents [$(H_2N)_2C$═C; **10c**] differently influence the partial aromaticity of the two ring moieties in **10c**. While in the three-membered ring moiety it is reduced, the partial aromaticity of the five-membered ring moiety is increased with respect to **10a** in agreement with the electron releasing character of the NH_2 substituents (electron flow into partial 6*π*-aromaticity increases while 2*π*-aromaticity is reduced appropriately). The same effects are expected in **10d**; however, due to steric hindrance, the compound is heavily twisted and hereby the expected *π*-electron flow at least partly hindered. Since the contribution of both resonance structures **14** and **15** (Scheme 5) stabilize the mesoionic structures **10**, the changes in partial aromaticity of the ring fragments in **10a−e** are in complete agreement with the heats of hydrogenation (in Table 2) and thus in agreement with the corresponding conclusions concerning the aromaticity of these captodative vinylogs of calicene (vide supra). (iv) The remaining captodative vinylogs **10f−i** are more or less twisted and the expected effects more or less covered; only **10g** proves to be planar, and the addition of another terminal cyclopropenylidene moiety changes the spatial magnetic properties dramatically. For both the in-plane deshielding ICSS = −0.1 ppm and the shielding ICSS = +0.1 ppm below and above the planar molecule, distances *d*/Å similar to those in cyclopropenylium cation **18** and benzene **19** were obtained, and in case of the shielding ICSS, they are even larger. Obviously, conjugation between 2*π*- and 6*π*-aromatic moieties proves to be responsible for the effects observed.

3.3. Quantification of the Push−Pull Effect in the Fulvalene Vinylogs. Further, by application of the NBO analysis to the global minima structures of both the push−pull and captodative vinylogs (**7**, **10**) of calicene **2**, obtained from ab initio calculations at the DFT level of theory, the occupation quotient $\pi^*_{C=C}/\pi_{C=C}$ of the double bond inserted between the two ring moieties, which appears to be the most general criterion for quantifying the push−pull effect in push−pull alkenes,[31] was examined with respect to quantification of this push−pull effect in the compounds studied. This result is of especially great interest because the same investigation of fulvenes[30] and fulvalenes[6] was not successful, and actually, it is not clear yet why the occupation quotient $\pi^*_{C=C}/\pi_{C=C}$ of the C═C double bond, as the general criterion[32] for quantifying the push−pull effect in push−pull alkenes,[31] does fail to work for the latter two classes of compounds.

The behavior of both the push−pull (**7**) and captodative vinylogs (**10**) of calicene (**2**), however, proves to be straightforward. The occupation numbers of the bonding π- and antibonding π*-orbital of the interring C═C double bond in **7** and **10a**−**d**,**g**−**i** and the corresponding occupation coefficients $\pi^*_{C=C}/\pi_{C=C}$ are given (together with the corresponding C═C bond lengths) in Table 5; captodative vinylogs **10e**,**f** were not considered because of O═C and H_2Si═C instead of the interring C═C double bond, and **10c** was not included, because according to the NBO analysis, only structure **10c′** was obtained.



10c′

The occupation coefficient $\pi^*_{C=C}/\pi_{C=C}$ can be correlated with the bond length of the central C═C double bond; electron releasing (push) substituents donate π-electron density into the antibonding π*-orbital, and acceptor (pull) substituents withdraw π-electron density from the bonding π-orbital, both increasing the C═C bond length by decreasing the π-bond order. The correlation is given in Figure 4a; for visualizing the general nature of this dependence, in Figure 4b the same correlation is given, including additionally the values for ethylene and 1,1-dimethylethylene.

The structures of both the push−pull vinylog **7** and the captodative vinylogs **10** studied are of strong push−pull character; the quotients >0.2 obtained are otherwise obtained only for pronounced push−pull olefins with two acceptor substituents at one and two electron releasing substituents at the other carbon atom of the central C═C double bond.[31b,32] Of course, the effect is much larger in **7** (0.357) than in **10a** (0.220), however, still being strong.

The greatest push−pull effect is observed in the dicyano substituted captodative vinylog **10b** followed by the *c*-C_5H_4 analogue **10h**. Acceptor substituents (also, the additional *c*-C_5H_4 ring will attract π-bond order from the interring C═C double bond in order to complete the π-electron sextet for partial 6π-aromaticity), obviously, increase the push−pull character of the captodative vinylogs, while the electron releasing substituents in **10d**,**g**,**i** are of less influence. The push−pull character of these compounds is lower ($\pi^*_{C=C}/\pi_{C=C}$ = 0.255−0.300) but not as small as that obtained for the nonsubstituted reference compound **10a** (0.220). These results lead to two conclusions. (i) Both electron withdrawing and electron releasing substituents at the interring C═C double bond increase the push−pull character of the captodative vinylogs **10**; this conclusion proves to be in complete agreement with aromaticity estimations of the compound **10** based on hydrogenation energies (vide supra). (ii) The effect is larger in the case of acceptor (pull) substituents; obviously, the decrease of the $\pi_{C=C}$ occupation is of stronger influence than an increase of the $\pi^*_{C=C}$ occupation.

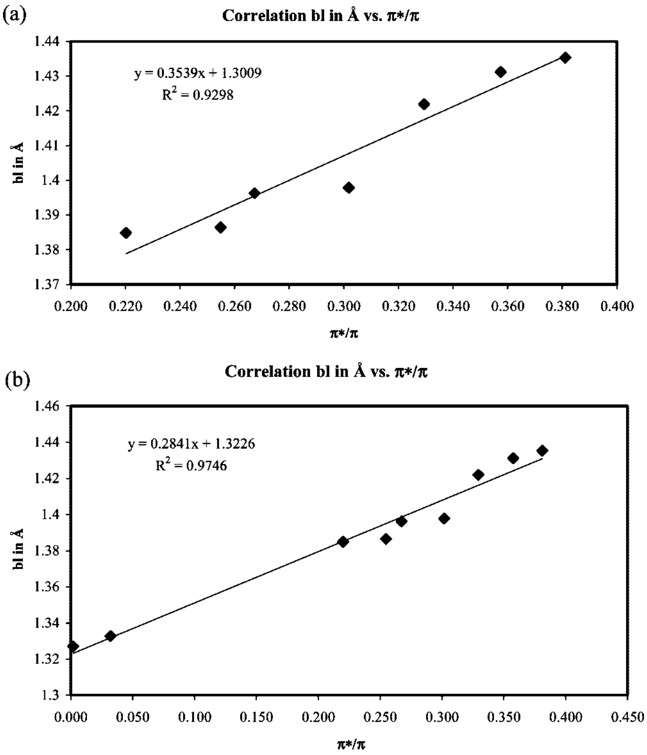


Figure 4. Correlation of the bond lengths bl/Å of the interring C═C double with the occupation coefficient $\pi_{C=C}/\pi^*_{C=C}$ in **7** and **10a**−**d**,**g**,**h** (a) and the same correlation including the corresponding values of ethylene and 1,1-dimethylethylene.

4. Conclusions

Application of structural, energetic, and magnetic criteria of aromaticity to the push−pull (vicinal) and captodative (geminal) vinylogs of calicene showed them to possess partial aromaticity. The molecule of the vicinal vinylog of calicene, compound **7**, is fully planar, and the two unsaturated rings are effectively conjugated through the central C−C bond, which has partial double character and is shortened with respect to, e.g., 1,3-butadiene. Its aromaticity assessed from the corresponding homodesmotic reactions is comparable to that of calicene and may be called push−pull aromaticity. Placing the two unsaturated ring moieties into the geminal position of the ethylene molecule gives rise to the mesoionic compound **10a** possessing the hitherto unknown type of aromaticity, captodative aromaticity. Molecule **10a** is fully planar, having no covalent bond linking the ipso-carbon atoms of the two rings, and clearly distinct from its isomer with such a bond, dispirocyclic molecule **9**. In the gas phase, it is less stable by ~3 kcal/mol than its dispirocyclic isomer, but in DMSO solution, it is computed to become more stable by >5 kcal/mol. The presence of both the double bond and the two aromatic ring moieties in the geminal position of this bond is a necessary and sufficient condition. If any of these conditions is not satisfied, the structure does not correspond to a minimum on the potential energy surface, at least in the gas phase.

Spatial magnetic properties of the push−pull and captodative vinylogs of calicene were calculated as TSNMRS, visualized as ICSS of various size and sign and employed to quantify the partial aromaticity in the three- and five-membered ring moieties of the compounds studied. Partial aromaticity of the isolated cyclopropylidene and pentadienylidene moieties **3a** and **3b** is higher than in the corresponding tris- (**16**) and pentafulvene (**17**) but lower than in the push−pull (**7**) and the captodative vinylogs (**10a**), and here again lower than in calicene (**2**). In addition, terminal substitution along the variety of captodative vinylogs **10** influences the partial aromaticity in the respective ring moieties; the partial aromaticity of **10a** ($CH_2{=}C$) and **10e** ($O{=}C$) is comparable. (−)M substituents reduce the partial aromaticity of both moieties, and (+)M substituents reduce the partial aromaticity of the three-membered ring moiety but increase the one of the five-membered ring moiety. Apparently, conjugation between 2π- and 6π-aromatic moieties is responsible for the effects observed.

In addition, the occupation quotient $\pi^*_{C=C}/\pi_{C=C}$ of the double bond inserted between the two ring moieties (by application of the NBO analysis), which appeared to be the most general criterion for quantifying the push−pull effect in push−pull alkenes,[31] was examined with respect to quantification of the push−pull effect in the compounds studied: both the push−pull **7** and the captodative vinylogs **10** have strong push−pull character (the one of **10**a is lower than in **7**). Acceptor substituents increase the push−pull character; electron releasing substituents are less influential, but the push−pull effect is still greater than in the reference compound **10a** ($CH_2{=}C$).

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Supporting Information Available: Relative energies, bond lengths, and bond angles of **1**−**12**. This material is available free of charge via Internet at http://pubs.acs.org.

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