Fine Tuning of the Mills–Nixon Effect. Influence of Substituents in some 1,2-Dihydrobenzocyclobutenes and Benzocyclobutenes

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A particular form of the 3-21G *ab initio* procedure is employed in estimating structural features of 1,2-dihydrobenzocyclobutenes and benzocyclobutenes. The Mills–Nixon (MN) type of bond shortening is identified in the parent hydrocarbon systems. Its extent can be amplified, diminished, completely cancelled or changed in sign depending on the electronegativity of the substituents at position 3. It is established that the underlying mechanism is that of rehybridization of the atoms of the benzene ring.

The Mills–Nixon effect[1] is a distortion of an aromatic nucleus when annelated to a small ring. It has been, and still is, a subject matter of continuous research interest. This is not unexpected since Mills–Nixon (MN) systems involve two important aspects of the chemistry of organic compounds—angular strain and aromaticity. Their interplay determines the structure and other physico-chemical properties of fused MN molecules involving a large aromatic part (benzene, naphthalene, *etc.*) and one or more fused small ring fragments. For the chemistry of these interesting compounds one should consult several available reviews.[2–6]

Structural features of the MN systems have aroused controversy which is not yet completely resolved. Some experimental data reveal double-bond localization within the aromatic moiety in the sense of the original MN hypothesis.[7–9] Some other authors believe that the MN type of bond fixation is a fiction and provide some experimental evidence which seems to support this contention.[10–14] In particular, serious doubts about the existence of the MN effect are raised by recent NMR measurements of chemical shifts[12] and four-bond proton–proton spin–spin coupling constants.[13,14]

Before proceeding further a word on terminology is appropriate here. The original MN postulate was related to a particular pattern of π-electron localization. By using a well known relation between π-bond orders and bond distances one can infer a variation of CC bond lengths in the benzene fragment. Our definition of the MN effect implies stretching of some bonds and shortening of others in the aromatic fragment caused by fusion to a (usually smaller) ring. Changing of bond distances of course affects many other observables, but we shall focus attention on structural features for the sake of simplicity. It is very important to keep in mind that an effect always refers to something which can be submitted to direct measurement. By the same token MN effects cannot be related to a particular spin pairing scheme of say π-electrons. We shall see later, for example, that π-electrons can be uniformly distributed over the benzene ring and yet its bond distances can exhibit significant variation.

Previous theoretical work on this topic was reviewed by us recently.[15] The most detailed *ab initio* studies performed so far[16–20] clearly indicate that the MN effect takes place in systems involving small annelated ring(s). An important outcome of these calculations is interpretation of the phenomenon. It appears that the underlying mechanism is rehybridization at the carbon junction atoms which is followed by π-electron localization. Secondly, if the π-electrons act in a concerted way as σ-electrons described by local hybrid orbitals, then a strong MN effect appears. On the other hand, if σ- and π-electrons counteract, then a mild MN deformation is observed.

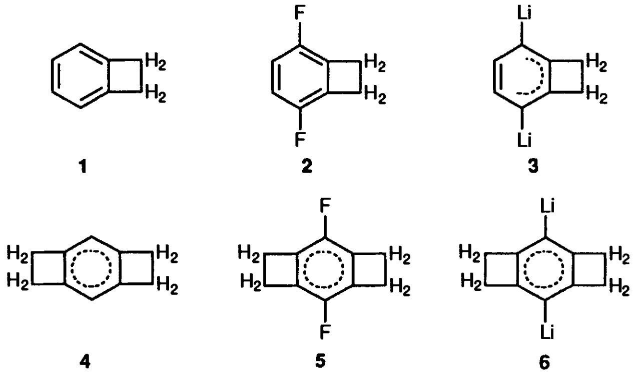


Fig. 1 Schematic representation of 1,2-dihydrobenzocyclobutene, 1,2,4,5-tetrahydrobenzo[1,2:4,5]dicyclobutene and their derivatives

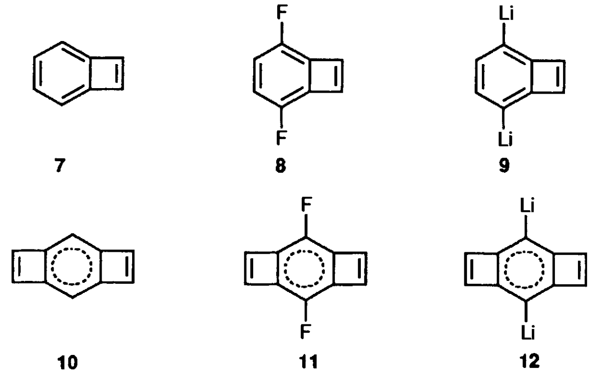


Fig. 2 Schematic representation of benzocyclobutene, benzo[1,2:4,5]-dicyclobutene and their derivatives

It is the aim of this paper to show that the extent of the MN distortion can be magnified or diminished by a judicious choice of substituents at particular sites of the molecule. In particular, we shall address the question of a complete cancellation of the MN effect. The examined systems encompass 1,2-dihydrobenzocyclobutenes and benzocyclobutenes, depicted in Figs. 1 and 2 respectively.

Theoretical Methodology

The adopted method should be economical and reliable. Previous calculations have shown that the *ab initio* 3-21G procedure is a good compromise between feasibility, computational costs and accuracy.[16,20] The quality of the structural data can be further increased by the following scaling procedure:[21] the 3-21G optimization of geometric parameters is performed first and then the scaled distances are obtained by using the linear relations eqns. (1)–(3).

$$d(\mathrm{C{=}C})_{\mathrm{sc}} = 0.896\, d(\mathrm{C{=}C})_{3\text{-}21\mathrm{G}} + 0.158\ \text{Å} \quad (1)$$

$$d(\mathrm{C{-}C})_{\mathrm{sc}} = 0.845\, d(\mathrm{C{-}C})_{3\text{-}21\mathrm{G}} + 0.223\ \text{Å} \quad (2)$$

$$d(\mathrm{C{-}F})_{\mathrm{sc}} = 1.052\, d(\mathrm{C{-}F})_{3\text{-}21\mathrm{G}} - 0.086\ \text{Å} \quad (3)$$

The numerical parameters in eqns. (1)–(3) are estimated by the least-squares method by employing experimental data for sets of characteristic small molecules.[21] The average absolute errors are *ca.* 0.005 Å implying that the predicted bond distances are pretty reliable. It appears that the empirical adjustments involved in eqns. (1)–(3) take care of a large portion of the correlation effect and the basis set defect. Let us illustrate this point by comparison of predicted bond distances in benzene by MP4(SDQ)/6-311 G** and $(3\text{-}21\mathrm{G})_{\mathrm{sc}}$ procedures. It should be pointed out that the 6-311 G** basis set is close to the Hartree–Fock limit. Additionally, the estimate of the electron correlation effect at the Møller–Plesset perturbation theory of the fourth-order should also be quite reliable. The calculated MP4(SDQ)/6-311 G** C–C distance of 1.3979 Å in benzene[21] is therefore very close to a true value. Interestingly, the $(3\text{-}21\mathrm{G})_{\mathrm{sc}}$ result is 1.399 Å thus being in excellent agreement with the high level theory. Although this kind of agreement is fortuitous, it shows rather nicely that the scaling procedure remedies to a considerable extent both (*a*) shortcomings of the small basis set and (*b*) the lack of the electron correlation.

It should also be stressed that single and double bonds are clearly distinguished in the studied systems. Hence, correlations (1) and (2) can be unambiguously applied.

As a final comment let us mention that use of scaled bond distances sometimes require a reoptimization of bond angles. This is achieved by the 3-21G computational procedure by keeping scaled bond distances of eqns. (1)–(3) constant. The differences between the final bond angles and original 3-21G values are very small as a rule.

Particular attention is focused on rationalization of the *ab initio* results. Modern interpretative quantum chemistry[22] may offer simple and transparent rationalization of the structural features of fused molecules. For this purpose we shall make use of hybridization parameters and bond orders of mobile π-electrons. There are several ways of determining the hybridization of local hybrid orbitals within the molecular orbital (MO) theory. Each of them defines its own scale of hybridization. One of the simplest is a recipe introduced by Trindle and Sinanoglu[23] which is based on the first-order density matrix. We have found that the minimal basis set semiempirical MNDO method yields hybridization parameters which are the closest to the classical notion of the local hybrid orbitals.[24] Concomitantly, the MNDO calculations are executed by using the fixed 3-21G scaled geometries given in Table 1.

Results and Discussion

The calculated structural data for 1,2-dihydrobenzocyclobutene and 1,2,4,5-tetrahydrobenzo[1,2:4,5]dicyclobutene and their difluoro and dilithium derivatives are presented in Table 1. Perusal of the calculated bond distances reveals a MN type of localization in the parent compound **1**. This effect can be amplified[19] by difluorination at positions C(3) as predicted by the qualitative Walsh–Bent rule, which states that hybrids possessing high p-character are directed toward electronegative atoms[23] (*vide infra*). Reversing the argument we can expect that the asymmetry in bond distances C(1)–C(1) and C(1)–C(3) will be smaller if electropositive lithium is substituted at the same positions in **3**. In fact, the two distances become equal (Table 1). The MN bond distance variation in **4** is smaller than in **1** as expected in view of the higher symmetry of this molecule. Difluorination at the central benzene moiety leads to an increased shortening of the *exo* C(1)–C(3) bond. Since the small ring dictates the properties of the composite system, *exo*-positions are defined relative to the smaller carbocycle. In contrast, lithium disubstitution not only cancels the MN effect, but leads to a tiny anti-MN bond distance change: the *exo* C(1)–C(3) bonds become longer than the annelated C(1)–C(1) bonds! It follows that the benzene ring distortion can be tuned by a judicious choice of the substituents attached to the aromatic moiety.

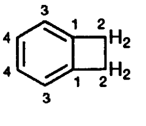
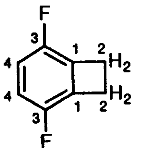
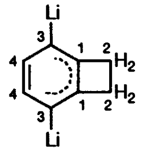
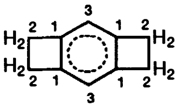
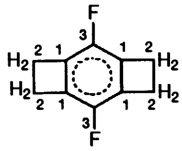
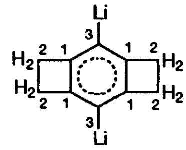
A survey of the data shows that the annelated C(1)–C(1) bond in **1** has lower s-character than an sp^2–sp^2 bond, whereas the opposite is the case for the *exo* C(1)–C(3) bond. This is compatible with their bond distances. The π-bond orders exhibit the same sort of change, but the variation is less pronounced. Notice that the π-bond order in benzene is 0.67. The carbon atom C(3) in **2** undergoes a rehybridization in accordance with the Walsh–Bent rule. The hybrid orbitals along the C(3)–F bond have hybridization parameters of 22.8–15.6 (in %) indicating that the carbon hybrid AO has less s-content than the sp^3 state. Consequently, the s-character is distributed over the C(1)–C(3) and C(3)–C(4) bonds leading to their shortening (by 0.01 Å). It is noteworthy that the π-bond orders do not contribute to these bond contractions. In fact, they are slightly smaller than the corresponding values in **1**. We note also in passing that fluorine bond hybridization is low (15.6%) in accordance with the high electronegativity of the F atom.

Quite the opposite situation is found in the C(3)–Li bond in **3**. The bond hybrid of the carbon atom is close to sp^1, whilst the other two hybrids emanating from the same carbon are of sp^3 type! Hence the *exo* C(1)–C(3) bond has an average s-character of 31.8% which should be compared with the s-content of 30.1% in the C(1)–C(1) annelated bond. Two remarks are in place here. It was shown that hybrids possessing the same hybridization have optimal bond overlapping.[25] Therefore 38.1–25.4 hybridization in the *exo* bond has less effective overlapping than hybrids possessing 30.1–30.1 s-character in the annelated bond. However, a difference in their π-bond orders makes these two bond distances virtually equal. Finally, we note that the hybridization in the Li atom has high s-content as expected for an electropositive atom.

The bond angles are compatible with the rehybridization picture. In this connection it is useful to recall that the C(1)–C(1) bond is bent inside the six-membered ring. This is plausible since hybrids placed at the same carbon atom make an angle larger than 90°. On the other hand, a hybrid of the C(1)–C(3) bond emanating from C(1) deviates out of the benzene ring. Since the deviation angles of the hybrids forming bent bonds should be as small as possible the angle C(1)–C(1)–C(3) opens up to *ca.* 122° in **1**. Concomitantly, the angle C(1)–C(3)–C(4) is diminished to *ca.* 116°. The changes induced by substitutions at the C(3) atoms are worthy of attention. In **2** the C(1)–C(3)–C(4) angle is increased to 118° in harmony with the increased s-character of the hybrids in question. In contrast, lithium substitution leads to considerable closing of the angle in accordance with its increased p-character. The rest of the data are easily understood and speak for themselves.

The related family of tetrahydrobenzodicyclobutenes follow the same pattern in structural properties and bonding

Table 1 Bond distances (in Å) and angles (in degrees) in 1,2-dihydrobenzocyclobutenes and 1,2,4,5-tetrahydrobenzo[1,2:4,5]dicyclobutenes as calculated by the 3-21 G scaled procedure, the corresponding hybridization parameters (in %) and π-bond orders

Molecule	Bond	Distance	Angle	s-Characters	π-bond order
 **1**	C(1)–C(1)	1.400	C(1)C(1)C(2) = 93.9	29.4–29.4	0.61
	C(1)–C(3)	1.386	C(1)C(3)C(4) = 116.3	37.2–32.4	0.70
	C(3)–C(4)	1.410	C(1)C(1)C(3) = 122.3	32.6–32.8	0.63
	C(4)–C(4)	1.401	HCH = 110.7	33.1–33.1	0.70
	C(1)–C(2)	1.523	HC(3)C(1) = 122.9	30.3–21.5	0.14
	C(2)–C(2)	1.574	HC(4)C(4) = 119.1	21.3–21.3	0.18
	C(3)–H	1.082		32.8	—
	C(2)–H	1.091		27.6	—
	C(4)–H	1.083		31.6	—
 **2**	C(1)–C(1)	1.398	C(1)C(1)C(2) = 93.4	29.9–29.9	0.62
	C(1)–C(3)	1.378	C(1)C(3)C(4) = 117.7	36.7–38.8	0.67
	C(3)–C(4)	1.399	C(1)C(1)C(3) = 121.4	38.9–32.0	0.62
	C(4)–C(4)	1.396	HCH = 110.9	33.7–33.7	0.90
	C(1)–C(2)	1.517	FC(3)C(1) = 122.7	30.8–21.3	0.14
	C(2)–C(2)	1.575	HC(4)C(4) = 120.3	21.2–21.2	0.08
	C(3)–F	1.341		22.8–15.6	0.23
	C(2)–H	1.090		27.6	—
	C(4)–H	1.080		31.9	—
 **3**	C(1)–C(1)	1.403	C(1)C(1)C(2) = 93	30.1–30.1	0.61
	C(1)–C(3)	1.402	C(1)C(3)C(4) = 110.5	38.1–25.4	0.68
	C(3)–C(4)	1.432	C(1)C(1)C(3) = 125.2	25.5–33.7	0.62
	C(4)–C(4)	1.405	HCH = 110.2	33.3–33.3	0.70
	C(1)–C(2)	1.529	LiC(3)C(1) = 123.2	28.6–22.2	0.14
	C(2)–C(2)	1.573	HC(4)C(4) = 116.7	21.5–21.5	0.08
	C(3)–Li	1.987		47.2–50.9	0.18
	C(2)–H	1.094		26.8	—
	C(4)–H	1.089		30.3	—
 **4**	C(1)–C(1)	1.403	C(1)C(1)C(2) = 93.2	29.9–29.9	0.65
	C(1)–C(3)	1.396	C(1)C(3)C(1) = 112.8	37.2–32.4	0.67
	C(1)–C(2)	1.523	C(1)C(1)C(3) = 123.6	30.1–21.6	0.14
	C(2)–C(2)	1.572	HCH = 110.6	21.3–21.3	0.08
	C(3)–H	1.082	HC(3)C(1) = 123.6	33.4	—
	C(2)–H	1.091		27.4	—
 **5**	C(1)–C(1)	1.400	C(1)C(1)C(2) = 93.3	30.4–30.4	0.65
	C(1)–C(3)	1.388	C(1)C(3)C(1) = 114.4	36.5–38.9	0.65
	C(1)–C(2)	1.516	C(1)C(1)C(3) = 122.8	30.6–20.4	0.12
	C(2)–C(2)	1.573	HCH = 110.8	21.3–21.3	0.08
	C(3)–F	1.338	FC(3)C(1) = 122.8	23.2–15.7	0.23
	C(2)–H	1.090		27.5	—
 **6**	C(1)–C(1)	1.409	C(1)C(1)C(2) = 93.1	30.3–30.3	0.64
	C(1)–C(3)	1.413	C(1)C(3)C(1) = 107.6	37.9–25.2	0.65
	C(1)–C(2)	1.529	C(1)C(1)C(3) = 126.2	28.5–22.3	0.14
	C(2)–C(2)	1.572	HCH = 110.1	21.5–21.5	0.08
	C(3)–Li	1.989	LiC(3)C(1) = 126.2	47.9–50.6	0.18
	C(2)–H	1.094		26.8	—

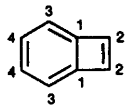
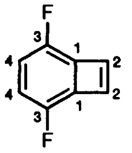
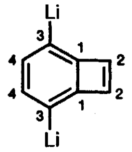
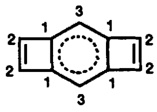
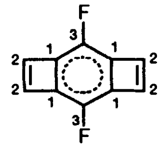
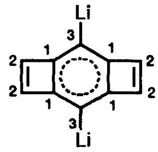
parameters as mentioned above (Table 1). Hence we shall omit a detailed discussion. However, it should be stressed that π-bond orders are evenly distributed around the benzene ring, closely approaching the free-benzene value. Hence, the variation of bond distances is entirely due to rehybridization.

As a final comment it should be emphasized that the hybridization parameters are to a high degree transferable. They reproduce the most striking features of characteristic local fragments being rather insensitive to fine details and smaller changes. Hence they successfully describe small fragments which can be used as building blocks for larger systems. This is of great conceptual importance.

There are several ways of increasing the extent of MN localization. Since this type of distortion of the benzene moiety arises because of the rehybridization of the carbon junction atoms, an obvious manner would be to increase the angular deformation by fusion of a smaller ring. This is achieved *e.g.* by annelation of a cyclobutene moiety. The angle C(1)–C(1)–C(2) in **7** then becomes smaller and the rehybridization effect is more pronounced. At the same time, the additional π-bond should affect the aromatic sextet in the sense of increasing its localization exactly in the MN pattern. Somewhat surprisingly, model calculations have shown that the former effect is much more important, and that the rehybridization alone leads to appreciable π-electron localization.[20] Addition of two additional 'antiaromatic' π-electrons provides a small correction in the same direction.

The calculated structural and bonding parameters for a series of benzocyclobutenes and benzo[1,2:4,5]cyclobutenes are given in Table 2. The MN effect is highly pronounced in **7**, further increased in **8** and somewhat diminished in **9**, as anticipated by considering the nature of the substituents. All changes are compatible with higher rehybridization at the bond fusion atoms and widely different π-bond orders. The C(2)=C(2)

Table 2 Bond distances (in Å) and angles (in degrees) in benzocyclobutenes and benzo[1,2:4,5]dicyclobutenes as estimated by the 3-21 G scaled procedure, the corresponding hybridization parameters (in %) and π-bond orders

Molecule	Bond	Distance	Angle	s-Characters	π-Bond order
 **7**	C(1)–C(1)	1.435	C(1)C(1)C(2) = 88.5	27.8–27.8	0.47
	C(1)–C(3)	1.360	C(1)C(3)C(4) = 115.6	39.5–33.4	0.82
	C(3)–C(4)	1.444	C(1)C(1)C(3) = 122.6	31.5–31.6	0.48
	C(4)–C(4)	1.376	HC(2)C(1) = 134.0	34.2–34.2	0.82
	C(1)–C(2)	1.529	HC(3)C(1) = 123.8	30.0–26.0	0.12
	C(2)–C(2)	1.356	HC(4)C(4) = 119.7	33.8–33.8	0.97
	C(3)–H	1.081		33.0	—
	C(4)–H	1.082		31.2	—
	C(2)–H	1.075		37.1	—
 **8**	C(1)–C(1)	1.433	C(1)C(1)C(2) = 88.5	28.2–28.2	0.46
	C(1)–C(3)	1.351	C(1)C(3)C(4) = 117.4	38.8–40.1	0.80
	C(3)–C(4)	1.435	C(1)C(1)C(3) = 121.6	37.6–30.8	0.46
	C(4)–C(4)	1.371	HC(2)C(1) = 133.4	34.7–34.7	0.82
	C(1)–C(2)	1.523	FC(3)C(1) = 124.4	30.6–25.8	0.12
	C(2)–C(2)	1.355		33.7–33.7	0.97
	C(3)–F	1.339		22.9–15.7	0.23
	C(4)–H	1.080		32.1	—
	C(2)–H	1.074		37.5	—
 **9**	C(1)–C(1)	1.441	C(1)C(1)C(2) = 88.4	30.1–30.1	0.45
	C(1)–C(3)	1.372	C(1)C(3)C(4) = 109.9	38.1–25.4	0.81
	C(3)–C(4)	1.473	C(1)C(1)C(3) = 125.7	25.5–33.7	0.45
	C(4)–C(4)	1.377	HC(2)C(1) = 135.2	33.3–33.3	0.83
	C(1)–C(2)	1.541	LiC(3)C(1) = 120.8	28.6–22.2	0.12
	C(2)–C(2)	1.355	HC(4)C(4) = 117.8	21.5–21.5	0.97
	C(3)–Li	1.982		47.2–50.9	0.19
	C(4)–H	1.088		30.3	—
	C(2)–H	1.080		36.9	—
 **10**	C(1)–C(1)	1.405	C(1)C(1)C(2) = 89.0	29.8–29.8	0.65
	C(1)–C(3)	1.394	C(1)C(3)C(4) = 112.2	38.3–32.4	0.67
	C(1)–C(2)	1.548	C(1)C(1)C(3) = 123.9	27.1–23.7	0.07
	C(2)–C(2)	1.351	HC(2)C(1) = 134.1	34.6–34.6	0.99
	C(3)–H	1.080	HC(3)C(1) = 123.9	33.5	—
	C(2)–H	1.075		37.3	—
 **11**	C(1)–C(1)	1.403	C(1)C(1)C(2) = 89.0	30.2–30.2	0.65
	C(1)–C(3)	1.387	C(1)C(3)C(1) = 113.6	37.6–38.9	0.65
	C(1)–C(2)	1.541	C(1)C(1)C(3) = 123.2	29.5–25.3	0.01
	C(2)–C(2)	1.350	HC(2)C(1) = 133.6	34.0–34.0	0.98
	C(3)–F	1.336	FC(3)C(1) = 123.2	23.4–15.8	0.23
	C(2)–H	1.074		37.7	—
 **12**	C(1)–C(1)	1.410	C(1)C(1)C(2) = 88.9	30.5–30.5	0.65
	C(1)–C(3)	1.412	C(1)C(3)C(1) = 106.6	39.0–25.2	0.65
	C(1)–C(2)	1.559	C(1)C(1)C(3) = 126.7	27.4–33.4	0.07
	C(2)–C(2)	1.351	HC(2)C(1) = 135.6	34.5–34.5	0.99
	C(3)–Li	1.984	LiC(3)C(1) = 126.7	48.3–50.5	0.18
	C(2)–H	1.080		36.0	—

bond remains almost completely localized as intuitively expected. We shall not dwell on details since the presented set of data is self-explanatory. Let us mention, however, that the π-electron distribution over the benzene moiety in benzodicyclobutenes is uniform and that the MN effect is completely cancelled in the lithium derivative **12**. Indeed, one obtains in **12** a highly symmetrical benzene fragment, although somewhat blown up. It is remarkable that substitutions at a particular position provide a mechanism for fine tuning of the MN (and anti-MN) effect.

Conclusions

The *ab initio* (3-21G)$_{SC}$ procedure shows that the MN effect occurs in 1,2-dihydrobenzocyclobutene and 1,2,4,5-tetrahydrobenzo[1,2:4,5]dicyclobutene, as well as in the corresponding benzocyclobutene systems. It can be amplified, diminished, completely cancelled or changed in sign depending on the electronegativity of the substituent at position 3. This is a remarkable finding since there is almost a dogma in organic chemistry about the extraordinary stability of the benzene nucleus. The present and our earlier calculations strongly indicate that benzene can be easily distorted by small ring(s) fusion and substitutions. A driving force for these deformations is rehybridization.

π-Electrons usually follow changes induced by rehybridization and act in a synergistic way. However, in some instances they act in the opposite direction leading to smaller MN effects, since rehybridization prevails as a rule. It follows that π-bond orders alone are not a good measure of the MN effect as supposed in a method based on measurements of the proton–proton spin–spin couplings over four bonds.[13,14] Hence conclusions drawn by this approach regarding the existence or absence of the MN effect are not justified in our opinion. In particular, we have shown in this work that there are systems where π-electrons are evenly distributed over the benzene moiety and yet its bond lengths exhibit non-negligible variation.

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