Theor Chim Acta (1993) 86: 343–351

Theoretica Chimica Acta

Theoretical study of Mills–Nixon effect in naphthocyclobutenes and -cyclobutadienes

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Received April 14, 1992/Accepted August 19, 1992

Summary. Structural features of some naphthocyclobutenes and naphtho(*b*)cyclobutadiene are studied by semiempirical and *ab-initio* procedures. It is found that Mills–Nixon (MN) effect is operative in all investigated molecules. Naphtho(*b*)cyclobutadiene exhibits the strongest MN type of deformation as anticipated. The calculated CC bond distances are in good accordance with available experimental data. They are rationalized by changes in hybridization parameters and π-bond orders. The rehybridization usually prevails in determining extent of the MN-deformation.

Key words: Fused molecules – Hybridization – Localization of electrons – Mills–Nixon effect – Rehybridization

1 Introduction

The Mills–Nixon effect is a phenomenon of the bond alternation in the benzene moiety when it is annelated to a small ring. The original hypothesis was put forward as early as 1930 [1] and since then it was a subject matter of debates and controversies. Some results were in favor of the MN postulate [2–11], whereas others have tried to deny it [12–18]. It should be pointed out that these findings depend rather strongly on the methods applied and the kind of the system under investigation. Since the MN systems exhibit appreciable amounts of angular strain and the so called aromaticity, sophisticated theoretical treatments are necessary for results which can be trusted. This is often precluded by the size of the MN systems which are relatively large as a rule. On the other hand, it is sometimes very difficult to synthetize some crown case compounds because of the high inherent (angular) strain. Additionally, the experimental evidence is often indirect (NMR) or obscured by the solid state effect, which is not easy to estimate. Finally, there is a lot of confusion produced by unjustified generalization: small deformations of the MN type found in one family of compounds or

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** Also at the Faculty of Science, The University of Zagreb, Marulićev trg. 19, 41000 Zagreb, Republic of Croatia a lack thereof is superficially extended to a general statement claiming that the MN effect is nonexistent in all molecules.

This state of affairs has prompted us to undertake a rather systematic study of the MN effect by *ab-initio* procedures employing carefully selected basis sets. We have shown that the MN effect takes place in benzocyclobutenes [19, 20], benzocyclobutadienes [21] and benzocyclopropenes [22]. It was found that the key mechanism leading to MN distortion is rehybridization at the carbon junction atoms. The π-electron redistribution follows the σ-skeleton deformation, usually in a cooperative way thus causing a strong MN localization. However, π-electrons sometimes counteract the σ-skeleton rehybridization leading to a weak MN effect or even to an anti-MN effect [23]. A particularly important outcome of our calculations is a fact that the MN effect can be tuned by a judicious choice of substituents placed at particular positions in molecules [22, 23]. For a review of the most recent theoretical results the reader is encouraged to consult Ref. [24].

In this paper we extend our studies to several naphtho(*a* and *b*)cyclobutenes and naphtho(*b*)cyclobutadiene (Fig. 1). Namely, there is nothing sacrosanct about the benzene moiety in the MN systems and the same sort of deformation should be found in larger aromatic systems fused to small rings. In fact, the available x-ray data show a mild MN localization in naphtho(*b*)cyclobutene [5]. The present theoretical results support the existing findings, provide a simple interpretation of the observed and calculated features and discuss structures and bonding in some related systems.

2 Theoretical approach

Adopted theoretical procedure should be the best possible compromise between accuracy and practical requirements (feasibility dictated by the size of the molecule, costs etc.). We have shown that *ab-initio* approach employing 3-21G basis set satisfactorily describes the main structural features of planar hydrocarbons [24]. Its performance can be further somewhat improved by some empirical adjustments leading to the scaled $(3\text{-}21G)_{SC}$ procedure. The latter is based on the 3-21G geometry optimization on a selection of characteristic molecules with known experimental structural parameters. The calculated 3-21G bond distances are then correlated with the experimental data. The least squares technique yields [25]:

$$d(\mathrm{C{-}C}) = 0.845\, d(\mathrm{C{-}C})_{3\text{-}21G} + 0.23\ \text{Å} \tag{1a}$$

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

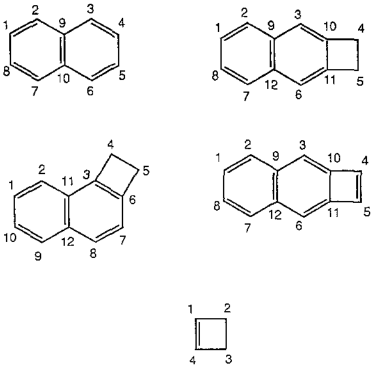


Fig. 1. Schematic representation of and numbering of atoms in the studied systems (from left to right): naphthalene, naphtho(*b*)cyclobutene, naphtho(*a*)cyclobutene, naphtho(*b*)cyclobutadiene, and cyclobutene

Since the studied molecules possess a small strained four-membered ring, it is also of interest to use a larger basis set involving a polarization function. Hence 6-31G* calculations are carried out for comparative purposes. Empirical MM2PI and semiempirical AM1 schemes are applied in order to test their performance in treating MN systems.

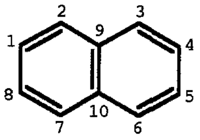
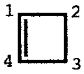
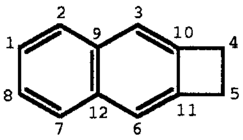
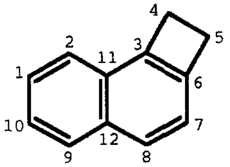
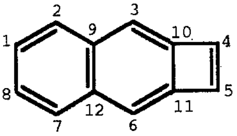
3 Results and discussion

3.1 Structural features

The most important bond distances are presented in Table 1. Survey of the data shows that the theoretical results are favorably compared with available experimental structural parameters for naphtho(*b*)cyclobutene and the fragment molecules naphthalene and cyclobutene. Average absolute errors for empirical MM2PI, semiempirical AM1, *ab-initio* 3-21G, 6-31G* and $(3\text{-}21G)_{SC}$ procedures are 0.009, 0.009, 0.012, 0.006 and 0.009 (in Å), respectively. Since experimental results are also subject to errors we are inclined to consider this kind of agreement as satisfactory. We note in passing that inclusion of the polarization function (6-31G*) introduces only a slight improvement and that performance of semiempirical schemes is better than expected.

More important than full agreement with experiment is variation of the bond distances within a particular molecule and between the corresponding bonds in the related molecules. They are usually given with better accuracy, but our main task is to provide rationalization for induced changes in structural parameters. Let us consider naphtho(*b*)cyclobutene first. The bond distances of bonds emanating from the carbon junction atoms are of particular importance (Fig. 2). They reflect the effect of fusion of the cyclobutene ring to the naphthalene skeleton. It is obvious that the *exo*-bond, e.g. C(3)–C(10), is shorter than in a free naphthalene. The shortening estimated by MM2PI, AM1, 3-21G, 6-31G*, $(3\text{-}21G)_{SC}$ and experimental methods assumes the following values: −0.012, −0.022, −0.013, −0.008, −0.012, and −0.017 Å, respectively. This is in line with the original MN postulate. The problem with the annelated C(10)–C(11) bonds is more subtle. Some authors are mislead by a fact that this bond is shorter than the corresponding bond in the parent naphthalene as indicated e.g. by experiment. However, the annelated bond differs from the free-naphthalene counterpart because it is highly strained. Its maximum electron density path is substantially bent inside the six-membered ring. The deviation angles of the hybrid orbitals in the related benzocyclobutene are $\approx 9°$ [20]. We note in passing that the *exo*-bonds are also bent (outside the ring) but to a considerably lesser extent. Hence, the interatomic distance of the annelated bond should be compared to a strained double bond like that found in a free cyclobutene. If the latter is accepted as a gauge, then a considerable lengthening of the annelated bond is observed: 0.077, 0.101, 0.089, 0.088, 0.080 and 0.065 Å as obtained by the MM2PI, AM1, 3-21G, 6-31G* and $(3\text{-}21G)_{SC}$ methods and experimental data respectively. This is also consistent with rationalization of the variation in bond distances by rehybridization (vide infra). We find a choice of the referent molecules crucial for understanding the MN effect [25] since an analogous situation was encountered earlier in the case of benzocyclopropenes [22]. An alternative reference point is provided by the average value of $d(C_1–C_4)$ and

Table 1. Comparison of theoretical CC bond distances estimated by MM2PI, AM1, 3-21G, (3-21G)$_{SC}$ and 6-31G* procedures with available experimental data (in Å)

Molecule	Bond	MM2PI	AM1	3-21G	6-31G*	(3-21G)$_{SC}$	Exp.
	1–2	1.378	1.373	1.357	1.358	1.374	1.371[a]
	2–9	1.424	1.422	1.419	1.421	1.429	1.422
	9–10	1.414	1.419	1.409	1.409	1.420	1.420
	1–8	1.417	1.416	1.414	1.417	1.425	1.412
	1–2	1.516	1.522	1.539	1.515	1.523	1.517[b]
	2–3	1.565	1.567	1.594	1.562	1.570	1.566
	1–4	1.340	1.354	1.326	1.322	1.346	1.342
	1–2	1.379	1.377	1.359	1.360	1.376	1.360[c]
	2–9	1.423	1.417	1.416	1.419	1.427	1.416
	9–12	1.428	1.421	1.417	1.419	1.428	1.432
	1–8	1.415	1.411	1.410	1.413	1.421	1.404
	3–9	1.435	1.440	1.433	1.430	1.442	1.423
	3–10	1.366	1.351	1.344	1.350	1.362	1.354
	10–11	1.397	1.455	1.415	1.410	1.426	1.407
	4–10	1.508	1.508	1.537	1.520	1.522	1.520
	4–5	1.600	1.575	1.560	1.572	1.541	1.565
	1–2	1.378	1.369	1.357	1.359	1.374	
	2–11	1.413	1.424	1.417	1.418	1.428	
	11–12	1.423	1.432	1.418	1.416	1.429	
	1–10	1.418	1.420	1.415	1.416	1.426	
	3–11	1.406	1.394	1.402	1.411	1.414	
	3–6	1.364	1.410	1.358	1.353	1.375	
	6–7	1.402	1.389	1.400	1.408	1.412	
	7–8	1.388	1.389	1.366	1.364	1.382	
	8–12	1.435	1.418	1.424	1.429	1.434	
	3–4	1.508	1.512	1.537	1.517	1.522	
	4–5	1.597	1.578	1.600	1.572	1.575	
	1–2	1.387	1.384	1.374	1.377	1.389	
	2–9	1.413	1.409	1.397	1.398	1.410	
	9–12	1.425	1.420	1.414	1.415	1.425	
	1–8	1.406	1.403	1.392	1.392	1.405	
	3–9	1.454	1.454	1.466	1.465	1.472	
	3–10	1.352	1.339	1.323	1.328	1.343	
	10–11	1.429	1.482	1.455	1.448	1.462	
	4–10	1.481	1.494	1.527	1.500	1.513	
	4–5	1.368	1.370	1.341	1.338	1.360	

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[a] Brock CP, Dunitz JD (1982) Acta Cryst B 38:2278

[b] Bak B, Led JJ, Nyggaard L, Rastrup-Andersen J, Sorensen CO (1969) J Mol Struct 3:369

[c] Crawford JL, Marsh RE (1973) Acta Cryst B 29:1238

[d] Korp JD, Bernal I (1979) J Am Chem Soc 111:4273

$d(C_1–C_8)$ bond distances in cyclobutene and naphthalene, respectively. A substantial lengthening in the fused naphtho(*b*)cyclobutene is obtained again. Taking into account the arguments presented above one can safely say that naphtho(*b*)cyclobutene exhibits a typical but mild MN deformation. A careful scrutiny of the theoretical results indicates that the bond distance C(3)–C(9) is lengthened relative to the corresponding value in naphthalene. At the same time the variation in the bond distances in the distal benzene ring is slightly diminished as if its aromaticity is somewhat increased. The effect is, however, very small. It is of some interest to compare these data with the results obtained in naphtho(*b*)cyclobutadiene. Although original MN systems encompass saturated fused carbocycles only, it is taken here for granted that they can embrace unsaturated (small) rings too. Then one can anticipate a more pronounced MN effect in naphtho(*b*)cyclobutadiene for two good reasons. In the first place, the angular distortion around the carbon junction atoms is higher in view of the smaller C(4)–C(10)–C(11) angle. This should lead to a stronger rehybridization. Secondly, the additional double bond C(4)–C(5) should contribute to a stronger π-electron localization in the "aromatic" 10-electron system of the naphthalene fragment. Since the VB structure with a cyclobutadiene moiety is strongly avoided, a substantial localization of the *exo*-bonds is expected. This conjecture is corroborated by actual calculations. The shortening of the *exo*-bonds is found to be: −0.026, −0.034, −0.034, −0.030 and −0.031 as estimated by the MM2PI, AM1, 3-21G, 6-31G* and $(3\text{-}21G)_{SC}$ methods, respectively. The corresponding lengthening of the annelated bond reads 0.089, 0.128, 0.129, 0.126 and 0.116, respectively. Obviously, the MN effect is considerably more pronounced in naphtho(*b*)cyclobutadiene. Further, lengthening of the C(3)–C(9) bond is larger than in naphtho(*b*)cyclobutene and a more even distribution of the bond distances within the distal benzene C(1)–C(2)–C(9)–C(12)–C(7)–C(8)–C(1) moiety is evident indicating its increased aromaticity.

Taking into account the most stable Kekulé structure of naphthalene, an interesting counteraction of σ- and π-electrons can be predicted in naphtho(*a*)cyclobutene. The rehybridization effect (vide infra) will try to shorten C(3)–C(11) and C(6)–C(7) *exo*-bonds and to stretch the fused C(3)–C(6) bond. On the other hand, π-electrons will try to do just the opposite. Results (Table 1) show that the *exo*-bonds C(3)–C(11) (C(6)–C(7)) are shortened by −0.018 (−0.015), −0.028 (−0.027), −0.017 (−0.014), −0.010 (−0.009) and −0.015 (−0.013) Å relative to naphthalene as estimated by the MM2PI, AM1, 3-21G, 6-31G* and $(3\text{-}21G)_{SC}$ procedures, respectively. This is similar to contraction of the *exo*-bonds in naphtho(*b*)cyclobutene. The annelated bond is lengthened relative to the cyclobutene value by an extent which is roughly two times smaller than that enountered in naphtho(*b*)cyclobutene. Since σ- and π-electrons act synergistically in naphtho(*b*)cyclobutene, it is expected that this molecule is more stable than naphtho(*a*)cyclobutene. Calculations show that it is indeed the case although the difference in total energy is surprisingly very small: 1.3 and 0.3 kcal/mol as evidenced by 3-21G and 6-31G* basis sets, respectively.

3.2 *Interpretation of the* MN *distortion*

Notion of modified atoms in chemical environment proved useful in discussing various molecular properties [26, 27]. One of the most important descriptors of covalently bonded modified atoms is hybridization [28]. It is well known that substantial rehybridization takes place in small rings where the angular strain plays a dominant role in determining their physico-chemical properties. The same should hold in the considered molecules. The hybridization parameters (s-characters) employed here are extracted from the AM1 wavefunctions computed at the $(3\text{-}21G)_{SC}$ and 6-31G* geometries employing prescription suggested by Trindle and Sinanoglu [29]:

$$W_{2s}^{AB} = W_{s(AB)}/(1/2)W^{AB} \tag{2}$$

where W^{AB} is the total bond order of the A–B bond:

$$W^{AB} = 2\sum_{\mu}^{A}\sum_{\nu}^{B} P_{\mu\nu} \tag{3}$$

and $W_{s(AB)}$ is a portion of the $2s_A$ orbital involved in the A–B covalent bond:

$$W_{s(AB)} = \sum_{\nu}^{B} P_{2sA\nu} \tag{4}$$

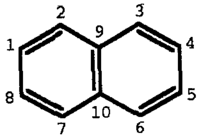
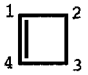
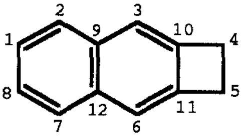
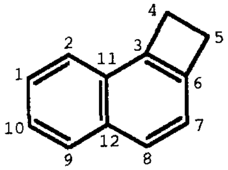
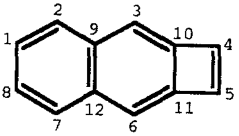
where summation is extended over atomic orbitals placed at the nucleus B. Here $P_{\mu\nu}$ denotes customary bond orders:

$$P_{\mu\nu} = 2\sum_{i}^{occ} C_{\mu i}C_{\nu i} \tag{5}$$

respectively. Hybrids' s-character, π-bond orders and two-center energies [30, 31] calculated also at the AM1 level are given in Table 2. It appears that the rehybridization at the carbon junction atoms is quite dramatic. Large deviation of the C(3)–C(10)–C(4) angle in naphtho(*b*)cyclobutene and -cyclobutadiene from the "ideal" 120° value has far reaching consequences. The s-character, measured relative to the fragment cyclobutene molecule, is shifted from the fused bond to adjacent *exo*-bonds. Hence the annelated C(10)–C(11) bond is described by hybrids possessing s-content of 28.5–28.5(%) which is close to *sp*(3)-*sp*(3) hybridization. The hybrid placed at the C(10) atom directed toward C(3) atom has s-character as high as 38.6%. Simultaneously, the hybrid pointing to the C(4) atom has s-content of 32.2% which is very high for a C–C single bond belonging to the cyclobutene ring. Comparison of the hybridization indices for $(3\text{-}21G)_{SC}$ and 6-31G* geometries shows that they are not very sensitive to small changes in bond distances. The same holds for π-bond orders and two-center bond energies. In addition to the increased p-character in the fused bond, there is a dramatic decrease of its π-bond order relative to cyclobutene (by 0.5). Hence a dramatic increase in the bond length is easily understood. The rest of the bond orders in naphtho(*b*)cyclobutene is very similar to those in naphthalene. There is a slight increase in the bond-order in *exo*-bonds by 0.03 and a decrease in their adjacent bonds C(3)–C(9) by −0.03. The former acts in the same direction as a rehybridization leading to the Mills–Nixon type of shortening of the *exo*-bonds. It is obvious, however, that MN deformation is much more influenced by the rehybridization than by π-electrons. We note in passing that C(4)–C(10) and C(4)–C(5) bonds have very low π-bond orders meaning that they are essentially single bonds. Concomitantly, the relationship (1a) was employed in estimating $(3\text{-}21G)_{SC}$ bond distances.

Hybridization in naphtho(*b*)cyclobutadiene follows the same pattern as in naphtho(*b*)cyclobutene, but the shift of the s-character from the fused C(10)–C(11) bond to C(3)–C(10) and C(10)–C(4) bonds is more pronounced. Concomitantly, the π-electron density is redistributed and shifted toward a distal

Table 2. AM1/(3-21G)$_{SC}$ s-characters, π bond orders and bicentric energy terms (in eV)[a]

Molecule	Bonds	s-characters %	π bond order	E_{AB} (eV)
	1–2	33.4–33.8 (33.1–33.6)	0.78 (0.80)	−20.8 (−21.1)
	2–9	31.2–33.4 (30.6–33.0)	0.50 (0.49)	−17.8 (−17.8)
	9–10	32.7–32.7 (32.2–32.2)	0.60 (0.62)	−18.6 (−18.8)
	1–8	31.6–31.6 (30.9–30.9)	0.53 (0.51)	−18.0 (−17.8)
	1–2	26.5–22.1 (26.6–21.8)	0.16 (0.15)	−13.7 (−13.8)
	2–3	21.0–21.0 (20.8–20.8)	0.08 (0.08)	−12.7 (−12.8)
	1–4	34.1–34.1 (33.4–33.4)	0.97 (0.97)	−22.6 (−22.8)
	1–2	33.3–33.7 (33.0–33.6)	0.78 (0.79)	−20.8 (−21.0)
	2–9	31.3–33.3 (30.7–33.0)	0.52 (0.51)	−17.9 (−17.9)
	9–12	32.9–32.9 (32.4–32.4)	0.61 (0.62)	−18.6 (−18.7)
	1–8	31.5–31.5 (31.0–31.0)	0.54 (0.53)	−18.0 (−18.0)
	3–9	31.0–31.0 (30.7–32.9)	0.47 (0.47)	−17.4 (−17.5)
	3–10	33.4–38.6 (32.9–37.7)	0.81 (0.80)	−21.4 (−21.4)
	10–11	28.5–28.5 (28.7–28.7)	0.47 (0.48)	−16.6 (−16.8)
	4–10	21.3–32.2 (21.1–30.7)	0.15 (0.15)	−13.8 (−13.8)
	4–5	21.6–21.6 (21.1–21.1)	0.09 (0.09)	−13.0 (−13.0)
	1–2	33.7–34.2 (33.1–33.6)	0.80 (0.79)	−21.1 (−21.1)
	2–11	30.7–34.0 (30.5–33.7)	0.49 (0.49)	−17.7 (−17.8)
	11–12	32.6–32.6 (32.4–32.3)	0.59 (0.61)	−18.4 (−18.6)
	1–10	31.3–31.3 (31.0–31.0)	0.51 (0.52)	−17.7 (−17.9)
	3–11	36.1–33.1 (35.0–32.4)	0.52 (0.50)	−18.2 (−18.0)
	3–6	31.2–30.8 (31.8–31.2)	0.75 (0.76)	−19.6 (−20.0)
	6–7	36.5–30.8 (35.4–30.2)	0.55 (0.52)	−18.3 (−18.1)
	7–8	33.7–33.9 (33.3–33.7)	0.77 (0.79)	−20.6 (−21.0)
	8–12	31.5–33.8 (30.6–33.1)	0.52 (0.50)	−18.0 (−17.8)
	3–4	32.0–21.4 (30.4–21.2)	0.15 (0.15)	−13.8 (−13.8)
	4–5	21.4–21.4 (20.9–20.9)	0.08 (0.08)	−12.9 (−12.9)
	1–2	32.8–33.3 (32.3–33.0)	0.71 (0.71)	−20.0 (−20.1)
	2–9	31.7–34.1 (31.5–33.8)	0.60 (0.60)	−18.7 (−18.9)
	9–12	33.2–33.2 (32.6–32.6)	0.62 (0.62)	−18.7 (−18.8)
	1–8	32.2–32.9 (31.7–31.7)	0.61 (0.62)	−18.8 (−18.9)
	3–9	30.0–32.0 (29.8–31.8)	0.36 (0.35)	−16.2 (−16.3)
	3–10	34.2–40.7 (33.5–39.5)	0.88 (0.88)	−22.5 (−22.6)
	10–11	26.1–26.1 (26.8–26.8)	0.34 (0.34)	−15.0 (−15.3)
	4–10	25.6–33.0 (25.7–30.8)	0.17 (0.17)	−14.1 (−14.1)
	4–5	34.3–34.3 (33.2–33.2)	0.95 (0.95)	−22.4 (−22.6)

[a] Figures within parentheses are related to 6-31G* geometries

benzene ring. More specifically, the π-electron density along the annelated bond is depleted (relative to free naphthalene) by 0.2 e. This mixed density is shared equally by the *exo*-bonds C(3)–C(10) and C(6)–C(11). Analogously, the π-electron mixed density in C(3)–C(9) and C(6)–C(12) bonds is lowered by 2 × 0.14 e, an amount which is redistributed over the distal benzene CC skeleton in a way

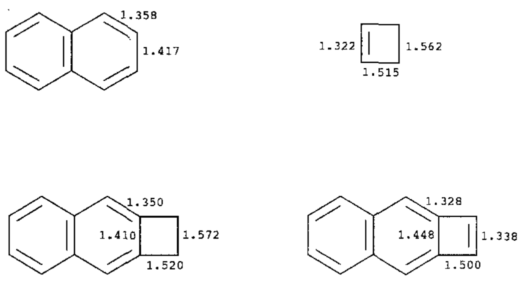


Fig. 2. Critical bond distances undergoing the largest changes upon fusion

which increases its aromaticity. It is worth mentioning that π-electrons tend to form two rather distinct subunits: distal benzene and 2,3-methylenecyclobutene moieties. One should also point out that in naphtho(*a*)cyclobutene a dominant π-electron coupling scheme of naphthalene remains roughly (but persistently) unchanged.

Bicentric energy terms E_{AB} provide a good qualitative index of the bond strength. Perusal of the data presented in Table 2 shows that variation of bicentric terms is compatible with changes in hybridization and π-bond orders. We omit a detailed discussion because of space consideration, but the given numbers speak for themselves.

4 Conclusion

It is shown that the MN-distortion is operative in naphthocyclobutenes and naphtho(*b*)cyclobutadiene. The effect is more pronounced in the latter molecule because of larger angular deformation of the four-membered ring and presence of the additional peripheral π-bond. The structural parameters are in good accordance with available experimental data. The lowest average absolute error is achieved by the 6-31G* basis set. However, variation in CC bond distance is well reproduced by all theoretical methods. Hence, MM2PI and AM1 schemes can be applied to related very large systems at least when qualitative information are necessary. The most striking structural features are interpreted in terms of rehybridization of the local hybrid orbitals and bond orders of mobile π-electrons in a transparent and intuitively simple way. Deformation of the aromatic fragment can be produced by concerted or counteractive interplay of σ- and π-electrons leading to difference in stability of isomers. Thus naphtho(*b*)cyclobutene is more stable than naphtho(*a*)cyclobutene because σ- and π-electrons act synergistically in the former molecule.

It has been stated that: "One of the most striking phenomena related to aromaticity is the unusual tendency of aromatic system to remain so" [32]. It is remarkable that aromatic systems can be so easily deformed to a considerable extent by fusion to small rings(s).

Acknowledgement. A part of this work has been performed at the Organisches Institut der Universität Heidelberg and one of us (Z.B.M.) would like to thank the Internationales Büro der Kernforschungsanlage Jülich for a financial support and Professor R. Gleiter for hospitality and useful discussions.

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