

Table IV

X	CI results <sup>a</sup>		SCF results <sup>a</sup>	
	$r_{XX}(X_6)$ , Å	$r_{XX}(X_2)$ , Å	$r_{XX}(X_6)$ , Å	$r_{XX}(X_2)$ , Å
H	0.9886	0.7351	0.9593	0.7122
Li( $\pi$ )	2.7718	2.1925	2.5095	2.0025
Li(s)	3.0717	2.8720	2.9093	2.6690
CH	1.4051	1.3407	1.3868	1.3060
N	1.3913	1.2928	1.3558	1.2475

<sup>a</sup>The  $X_2$  models for X = N, CH are HN=NH(t) and H<sub>2</sub>C=CH<sub>2</sub>, respectively.

#### IV. Conclusions

The extent of delocalization in 6-electron 6-center systems cannot serve as a criterion of stability of the delocalized state against a localizing distortion. The composition of the wave function, in terms of the character and weights of the contributing resonance structures, was found to yield no information regarding the stability or the preferred geometry of the delocalized electronic sextet. Extreme care must be exercised not to attach special importance to the contribution of a certain resonance structure or another, at least in these types of systems.

While undergoing delocalization, an electronic system must pay the price of electronic reshuffle or reorganization ( $G$  in Figure

(22) Virial theorem analysis leads to some surprising conclusions regarding the delocalization in benzene, see: Blaise, P.; Henri-Rousseau, O. *C. R. Hebd. Seance Acad. Sci., Ser. C* 1980, 1290, 69.

1, eq 6). Whenever this price is costly, the system would prefer to remain localized in a geometry that hinders electronic delocalization (10A). Only in certain systems with weak two-electron bonds (low  $\Delta E_T(X_2)$  and  $D(X_2)$ ) will the price of electronic reshuffle be low enough to afford delocalization. In such cases, delocalization of the electronic sextet would indeed be a driving force that will shape the molecular stability and geometry.<sup>34</sup> Our conceptual grasp of the role of electronic delocalization must accordingly be modified.

While there is no denying that benzene possesses a special stability,<sup>20</sup> our present studies raise the question whether it is really the  $\pi$  system that drives benzene to be a symmetric hexagonal species. Our preliminary calculations<sup>23</sup> show that indeed the  $\pi$  system, were it by itself, would have preferred a distorted localized structure. These results and others will be reported in future publications.<sup>23</sup>

**Acknowledgment.** The authors are grateful to J. M. Lefour and G. Ohanessian for assistance and discussions. Sason Shaik is grateful to the CNRS for a "poste rouge".

#### Appendix

Table IV gives the geometric parameters which were obtained by optimization.

(23) Hiberty, P. C.; Shaik, S. S.; Lefour, J. M.; Ohanessian, G., submitted for publication.

## The Valence-Bond Description of Conjugated Molecules. 4. Theoretical Study of the Mills–Nixon Effect, a Phenomenon of $\pi$ -Bond Localization in Small Ring Annelated Aromatics

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**Abstract:** The so-called Mills–Nixon effect, a phenomenon of  $\pi$ -bond localization in aromatic rings annelated by strained saturated rings, is studied by means of ab initio calculations of valence-bond type on benzocyclopropene and benzocyclobutene, in their equilibrium geometries calculated by using a gradient technique. In apparent discrepancy with an experimental work, recently published in this journal,<sup>1</sup> dealing with cyclobutane-annelated dihydropyrenes, our results evidence a significant Mills–Nixon effect. To understand its origin, additional calculations have been performed on benzocyclopropene and benzocyclobutene in standard geometries and in distorted benzenes, showing that the influences of cyclopropene and cyclobutene on aromatic rings are of different natures. Tendencies arising from these calculations and additional ones on naphtho[b]cyclopropene and naphtho[b]cyclobutene suggest a possible explanation for the absence of sizable Mills–Nixon effect in cyclobutane-annelated dihydropyrene.

#### I. Introduction

Over 50 years ago, Mills and Nixon<sup>2</sup> postulated that the fusion of a small-ring compound on a benzene molecule induces a reorganization of the resonance between the two Kekulé structures, i.e., causes a partial  $\pi$ -bond localization as shown in the following scheme:



Their aim was to rationalize certain differences in the chemical reactivities in indan and tetralin. However, the experimental data

on which the effect was based were subsequently shown to be ambiguous,<sup>3</sup> and the proposal of Mills and Nixon initiated a long series of experimental and theoretical studies on related molecules, trying to prove or disprove the effect.

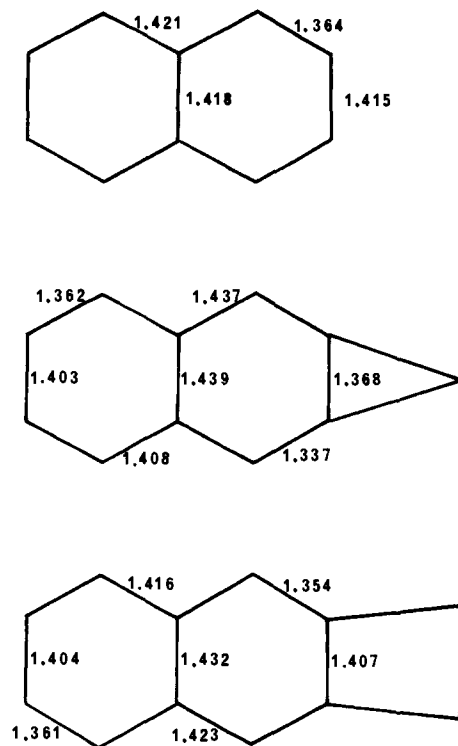
While benzocyclopropene and benzocyclobutene still remain difficult to observe, an extensive series of large annelated aromatics have now been synthesized.<sup>4</sup> A number of experimental techniques have been used to study their properties, such as X-ray crystallography and NMR and UV spectroscopies. Both the physical and chemical properties of many of these compounds were found to be sensitive to annelation, still no definite answer to the question of double-bond localization could be given.

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(2) Mills, W. H.; Nixon, I. G. *J. Chem. Soc.* 1930, 2510.

(4) (a) Korp, J. D.; Bernal, I. *J. Am. Chem. Soc.* 1979, 101, 4273 and references therein. (b) A review of earlier work can be found: Halton, B. *Chem. Rev.* 1973, 73, 113.



**Figure 1.** Gradient-calculated equilibrium geometries for benzocyclopropene and benzocyclobutene. For both compounds, CH bond lengths have been found equal to 1.083 Å for the hydrogens attached to the benzene ring and 1.089 Å for the other ones.

The geometry was often used to predict changes in the weights of resonant structures, a bond shortening being associated with an increase of importance of the structure bearing a double bond on that particular linkage. It has already been recognized<sup>5</sup> that this reasoning is often inappropriate since in a substituted benzocyclopropene, for example,<sup>6</sup> the bond common to the benzene and cyclopropene rings and the two adjacent bonds all are shortened with respect to their length in benzene, while all three cannot have more double-bond character than they have in benzene itself. It is thus difficult to separate the geometric distortions which are caused by the strained  $\sigma$  bonds from the ones due to  $\pi$ -bond localization. In some cases, however, like that of the annelated naphthalenes,<sup>7</sup> some geometric distortions can apparently be attributed to a  $\pi$ -bond-localization effect since they are observed far from the small ring and thus cannot be explained in terms of  $\sigma$  distortion (see Figure 1).

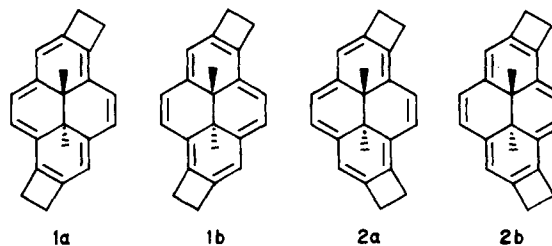
On the theoretical side, a number of studies have appeared, leading to a controversy on the direction of double-bond fixation or its existence itself. Streitwieser<sup>8</sup> has explained the observed data for the protodetritiation kinetics of some small-ring annelated aromatics on the basis of a "rehybridization effect model", in which the  $\sigma$  bonds  $\alpha$  to the strained ring have a large s character, thus resulting in an increased electron density of the  $\alpha$  carbons with respect to the  $\beta$  carbons. This explanation does not invoke any bond-localization effect.

Other theoretical treatments consisted of an optimization of the molecular geometry of annelated benzenes, which was believed to be enough to infer conclusions regarding the Mills–Nixon effect. The first attempt of this kind was made by Coulson and Longuet-Higgins,<sup>9</sup> parametrizing the resonance integrals in the Hückel

molecular Orbitals (HMO) method against geometric deformations. Their optimum structure for indan is surprisingly reasonable, as compared with the geometry of larger aromatics that were determined later, when one considers the crudeness of the approximations of the HMO method. The relative lengths of the various CC bonds led Longuet-Higgins and Coulson to conclude to an anti-Mills–Nixon effect.

Another calculation of this kind has been performed by Cheung, Cooper, and Manatt<sup>10</sup> using the CNDO/2 method, resulting in an optimum geometry at variance with that of Longuet-Higgins and Coulson. The striking feature of their results was the predicted lengthening of the junction bond, as well as a shortening of the two adjacent bonds, with respect to benzene bond lengths. Thus they were able to conclude to a bond-localization effect consistent with the original prediction of Mills and Nixon. In addition, they reported sizable variations in the six-membered-ring bond orders from benzene to benzocyclopropene, in agreement with the same effect. Benzocyclobutene was also studied and shown to display the same effect, although to a lesser extent. Other calculations of the SCC-EH (self consistent charge-extended Hückel) type further supported these results. However, these calculated equilibrium geometries seem contradictory enough with experimental findings to cast some doubts on the validity of these semiempirical results, all the more as the CNDO/2 method is now known to be inappropriate for the calculation of geometrical features.

Until very recently, it thus seemed that there existed no reliable calculation allowing any conclusion about the Mills–Nixon (MN) effect, while this effect was, on the other hand, apparently supported by some X-ray experiments in the case of annelated naphthalenes. But a new important element has recently appeared in this journal with the experimental work of Mitchell et al.,<sup>1</sup> who studied the MN effect in the case of dimethyldihydropyrenes annelated by two cyclobutanes (**1** and **2**). As one of these com-



ounds, **1**, is prevented from displaying any bond-localization effect for symmetry while **2** is not, any difference between the bond orders of the macrocyclic ring bonds can be related to the MN effect. Mitchell et al. used a correlation established previously<sup>11</sup> between the chemical shifts of the internal protons in a series of benzannulated dihydropyrenes and the average deviations of  $\pi$ -SCF-bond orders of the macrocyclic ring bonds from the parent dihydropyrene value, as calculated by the Pariser–Parr–Pople (PPP) method. They thus derived an empirical equation which was shown to possess a nice predictive power for other members of the series, errors being less than 0.5 ppm. Chemical shifts were found to be very similar in compounds **1** and **2**, thus indicating a maximum bond-order deviation of 0.0044 between the macrocyclic rings of these compounds. This led the authors to conclude to the absence of any significant  $\pi$ -bond-localizing MN effect.

It is our opinion, however, that the general question of the Mills–Nixon effect is still open. Indeed, there are still no experimental data concerning the annelated benzenes, the very compounds studied by Mills and Nixon. On the other hand, the semiempirical bond-order calculation of Manatt and co-workers is conflicting with Mitchell's chemical shifts which were, in other circumstances, in agreement with semiempirically calculated bond

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orders. Lastly, X-ray experiments on annelated naphthalenes seem coherent with a  $\pi$ -bond-localizing effect. Therefore, as Mitchell's experiments have been run for cyclobutane-annelated 14-membered rings, two questions arise: (i) can we generalize Mitchell's conclusion to other aromatic rings, and (ii) can we generalize the same conclusions to other annelating small rings, like cyclopropane? While the present paper is primarily devoted to a detailed study of the original Mills-Nixon proposal, i.e., the  $\pi$ -bond localization in annelated benzenes, an answer to the above questions will be attempted below.

The most direct way to estimate relative weights of resonance structures, or structural weights, is to perform a reliable calculation of valence bond (VB) type. The accurate determination of the geometric distortions induced by annelation is, of course, necessary since the structural weights depend partially on it, but it is by no means sufficient for reasons already discussed above. Calculation of bond orders is also insufficient, especially in large compounds, because a large number of structures containing one "long bond" (diradical structures) are present<sup>12</sup> and also contribute to bond orders by their short bonds, in an extent unpredictable a priori. In a VB calculation, on the other hand, one can calculate rigorous structural weights<sup>13</sup> which are coherent<sup>14</sup> with the Mulliken population analysis,<sup>15</sup> itself in good agreement with NMR experimental estimations of net charges. We therefore undertook such calculations, at the ab initio level, using a method that we briefly recall in the next section. Results for benzocyclopropene and benzocyclobutene will be presented in section III, together with their interpretation, and a discussion of their differences. Extension to larger aromatics is made in section IV, with calculations on naphtho[b]cyclopropene and naphtho[b]cyclobutene, and we end up with tentative extrapolations to higher analogues, including some predictions for yet unsynthesized molecules.

## II. Theoretical Methods

We have used a method developed previously,<sup>16</sup> aimed at avoiding the thorny problem of the calculation of the Hamiltonian matrix elements between non-orthogonal determinants. The procedure starts with a standard SCF calculation; then its  $\pi$  part, which is the only one of interest here, is projected onto a complete basis of valence bond structures. It is worth insisting on the fact that this MO vs. VB projection does not contain any approximation of its own. We thus obtain an *exact* VB description of the SCF  $\pi$  wave functions. By doing this, we gain a much more detailed description of the molecule than with a single SCF calculation, which only gives net charges and bond orders as information regarding the bonding structure.

From a more formal point of view, the idea behind the transformation originates in the well-known equivalence of the MO and VB methods if a complete configuration interaction (CI) treatment is achieved for both.<sup>17</sup> It would then be possible to obtain exact VB wave functions (within atomic orbital basis set limitations) if the projections were performed after full CI in the MO frame. This, of course, is out of reach with present computational possibilities. However, we have shown in the first papers of this series<sup>18</sup> that the relative weights of covalent structures with no long bonds (often called "classical structures") are already satisfactorily calculated at the SCF level. The role of a subsequent CI treatment would be to adjust the importance of ionic (which are overestimated at the SCF level) and Dewar-type covalent structures (which are underestimated) as compared with the classical ones. We can therefore limit ourselves to the SCF weights, inasmuch as relative rather

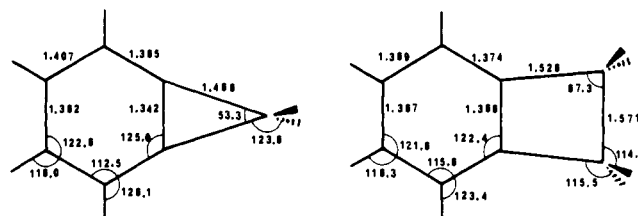


Figure 2. Experimental bond lengths for naphthalene, naphtho[b]-cyclopropene and naphtho[b]cyclobutene (see ref 7).

than absolute weights of Kekulé-type structures are concerned in the MN effect.

Hyperconjugation can take place between the  $\text{CH}_2$  group(s) and the  $\pi$  orbitals of the aromatic ring. We have therefore taken the out-of-plane hydrogens into account, by replacing their respective  $1_{\text{SA}}$  and  $1_{\text{SB}}$  orbitals by a  $\pi$ -type function ( $1_{\text{SA}} - 1_{\text{SB}}$ ); this of course is not an approximation, but a practical way to include the  $\pi_{\text{CH}_2}$  orbitals in the VB treatment.

As will appear in the next section, our results for benzocyclopropene and benzocyclobutene, concluding to the existence of a significant Mills-Nixon effect, promoted us to perform some additional calculations on larger molecules in order to explain the apparent disagreement with the experimental results of Mitchell et al.<sup>1</sup> However, the limitations of our program to 10 orbitals at most were attained with benzocyclobutene. Therefore, to be able to study naphthalene derivatives, we had to reduce the dimension of the system of  $\pi$  orbitals to that of the naphthalene moiety. This can be done by means of a localization procedure, which leaves the total SCF wave function unchanged, but separates the  $\pi_{\text{CH}_2}$  orbitals from the other  $\pi$  orbitals. A necessary condition for this process to be effective is that the hyperconjugation between the  $\text{CH}_2$  group(s) and the aromatic ring be negligible; as will be seen in the next section, examination of our results for benzocyclopropene and benzocyclobutene shows that this condition is fulfilled. It is worth noting that this does not mean that the  $\text{CH}_2$  groups have a negligible influence on the aromatic ring; rather, the nature of this influence is best expressed as a polarization of the aromatic ring by the  $\text{CH}_2$  group(s), while there is practically no inter-ring bond or charge transfer. We thus localized the SCF wave functions of naphthalene derivatives, using Boys' criterion,<sup>19</sup> and projected on the VB basis the  $\pi$ -MOs reduced to their components on the aromatic ring, neglecting the small residual tails on the  $\text{CH}_2$  groups. This approximation has been tested in the case of benzocyclopropene, by comparison with the complete calculation, and shown to be quite satisfactory for our purpose; more details will be given in section IV.

All SCF calculations were performed with the MONSTERGAUSS series of programs.<sup>20</sup> The minimal STO-3G basis set<sup>21</sup> of atomic orbitals has been used throughout. Such calculations on conjugated hydrocarbons are well documented in the literature, and they display calculated properties in good agreement with experimental data as regards equilibrium geometries,<sup>22</sup> net charges, or dipole moment values.<sup>23</sup> In fact, the risk of using a minimal basis set is to miss the vertical correlation energy, i.e., to disfavor ionic situations, which is of no importance here since we compare the relative weights of neutral structures. Therefore, the trends that we search here should be reasonably reproduced at this level of theory.

## III. Benzocyclopropene and Benzocyclobutene

As there are no experimental geometries available for benzocyclopropene (BCP) and benzocyclobutene (BCB), we first determined the equilibrium structure of these compounds by using a gradient technique, at the ab initio level, in the minimal STO-3G basis set. This level of theory is known to be satisfactory for the optimization of geometrical parameters for conjugated molecules. The double-bond lengths are found slightly shorter than experimental values, but in a systematic way. As an example, the cyclobutene<sup>24</sup> and cyclopropene<sup>25</sup> double-bond lengths are found

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




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




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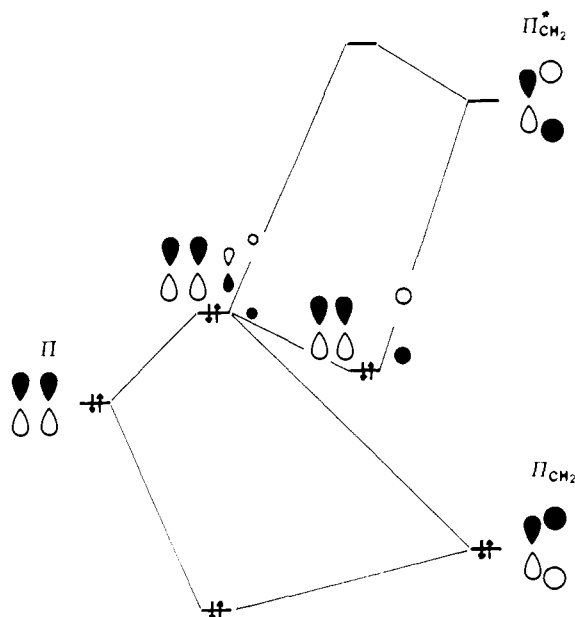
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**Table I.** Structural Weights for Benzocyclopropene and the Benzene Fragment Alone, Distorted as It Is in the Equilibrium Geometry of Benzocyclopropene

						structures displaying exocyclic bonds
BCP equil geometry	0.398	0.299	0.097	0.097	0.102	0.008
distorted benzene (as in BCP)	0.380	0.321	0.096	0.096	0.108	
BCP standard geometry	0.368	0.327	0.101	0.101	0.094	0.008

**Table II.** Structural Weights for Benzocyclobutene and the Benzene Fragment Alone, Distorted as It Is in the Equilibrium Geometry of Benzocyclobutene

						structures displaying exocyclic bonds
BCB equil geometry	0.395	0.298	0.099	0.099	0.097	0.013
distorted benzene (as in BCB)	0.397	0.305	0.099	0.099	0.100	
BCB standard geometry	0.348	0.343	0.100	0.100	0.097	0.013

**Figure 3.** Interaction of an ethylene highest occupied molecular orbital with an occupied  $\pi_{\text{CH}_2}$  orbital and a virtual  $\pi^*_{\text{CH}_2}$  orbital.

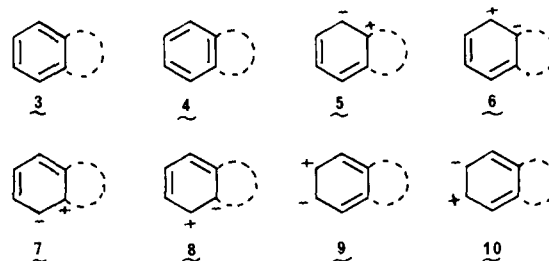
too short by 0.028 and 0.023 Å, in STO-3G calculations, while the C–C bond lengths in benzene are found too short by 0.01 Å, a value quite coherent with the previous ones since benzene has partial double bonds. Thus, there is no doubt that our geometry optimization faithfully reproduces the tendencies of benzene bond distortions upon annelation by strained rings.

The equilibrium geometries of BCP and BCB were optimized with the imposed  $C_{2v}$  symmetry. After completion of the geometry optimizations, final root-mean-square gradient lengths were 0.000 44 and 0.000 64 au for BCP and BCB, respectively. The results are displayed in Figure 2, and they show the following tendencies: when a cyclopropane is fused to a benzene ring, the junction bond is shortened with respect to its length in benzene, and the two adjacent C–C bonds are also significantly shortened; when a cyclobutane ring is fused, the junction bond lengths practically remain that of benzene. While the two adjacent bonds are moderately shortened. These tendencies are in qualitative agreement with the one experimentally observed in annelated naphthalenes (see Figure 1). It should be noted that, unlike BCP, BCB has the junction bond longer than the adjacent C–C bonds, and this difference between both compounds has some importance, as will be discussed below. Incidentally, we note that our geometry for BCP is very similar to that calculated at the Hückel level by Longuet-Higgins and Coulson for indan<sup>9</sup> and at large variance with the CNDO/2 result of Cheung et al.<sup>10</sup>

Using our optimized geometries, we have projected the SCF wave functions of BCP and BCB on complete basis sets of covalent

VB functions, by means of the method described in section II. The calculated structural weights, normalized to unity, of Kekulé and Dewar structures for BCP and BCB are displayed in the first rows of Tables I and II, respectively, along with the sum of the weights of structures displaying exocyclic bonds, i.e.,  $\pi$  bonds between the outer  $\pi_{\text{CH}_2}$  orbital(s) and a  $\pi$  orbital of the ring. These terms are in fact very weak, showing that there is no electron delocalization from the benzene ring to the small ring or vice versa.

It appears immediately, by inspection of Tables I and II, that a significant  $\pi$ -bond-localization effect exists in both BCP and BCB, in the direction predicted by Mills and Nixon, since the ratios of Kekulé structures 3:4 are 1.332 and 1.325, respectively. To establish this result more firmly, we have performed another VB analysis of BCP and BCB, now including in the VB basis all the monoionic structures deduced from covalent ones by replacing one covalent bond by a zwitterionic bond. As an example, the structural weight of Kekulé structure 3 is defined, in this calculation, as the sum of the weights of structures 3 and 5–10. Doing



this is equivalent to adding to each covalent bond its zwitterionic counterpart and defining a formal bond as partly covalent and partly ionic, as it is in reality (the  $\text{H}_2$  bond, for example, is 50% covalent and 50% ionic, at the SCF level, and 80% covalent and 20% ionic when electron correlation is introduced).

The results of this new series of calculations confirm the previous ones, since now the ratios of the weights of structures 3 and 4 are 1.301 and 1.292, respectively, for BCP and BCB. This agreement between both types of analysis, including the monoionic structures or not, is not surprising as we have already experienced it in a previous work,<sup>26</sup> and in what follows only the simplest technique will be used.

It is now interesting to try to understand the origin of the Mills–Nixon effect which we have established for annelated benzenes. A priori, two factors may be thought to intervene: (i) the geometric distortions induced by the strained ring at the level of the  $\sigma$  bonds of the benzene ring might favor one Kekulé structure with respect to the other one, and (ii) the exocyclic  $\pi_{\text{CH}_2}$  orbitals might interact with the benzene  $\pi$  orbitals, independently of any geometric distortions. To estimate the relative importance of these two factors, we have performed two new series of VB calculations. In the first series, whose results are displayed in the

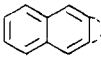
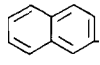
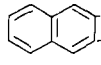
second rows of Tables I and II, we calculated and analyzed the wave functions of simple benzene molecules, with no strained rings attached to them, but having the geometries of BCP and BCB's benzene rings, respectively. In such calculations, any bond-localization effect can be interpreted as a consequence of geometric distortion alone. In the second series (see the third rows of Tables I and II), BCP and BCB are calculated and analyzed, using standard geometries for the benzene rings, i.e., C-C bond lengths equal to 1.40 Å. Now any  $\pi$ -bond-localization effect can be attributed to a nongeometrical effect, i.e., to the direct electronic influence of the CH<sub>2</sub> group(s).

Examination of Tables I and II shows that the factors responsible for the MN effect are not the same in BCP and BCB. In BCP, both geometric distortions and orbital interactions are important, leading to 3:4 weight ratios of 1.185 and 1.126, respectively, these two factors being approximately additive. In BCB, on the other hand, the orbital interactions seem to be of minor importance, only leading to a 3:4 weight ratio of 1.015, while the geometric effect is practically responsible for all the phenomenon, and twice as efficient as in BCP. The reason why the geometric effect is not very great in BCP, despite considerable distortions with respect to benzene, is that the junction bond is significantly shorter than the adjacent ones in BCP, unlike in BCB, and this opposes the MN effect by stabilizing structure 4.

The electronic effects of the CH<sub>2</sub> groups on the structure of the benzene ring can be explained most simply by the fact that the  $\pi_{\text{CH}_2}$  electrons, polarized toward the carbon  $\pi$ -p orbital, repel the bonding density of the ethylene moiety in Kekulé structure 3, while this repulsion does not exist in 4, with no  $\pi$  bond at the junction. This is of course true only if the CH<sub>2</sub> group is close enough to the middle of the junction bond, which is the case in BCP but not in BCB. To understand this interaction in more detail, let us consider the interaction of a doubly occupied  $\pi$  molecular orbital (MO) of an ethylene with  $\pi_{\text{CH}_2}$  and  $\pi^*_{\text{CH}_2}$  MOs respectively doubly occupied and unoccupied (see Figure 3). The ethylene  $\pi$ -MO first mixes with  $\pi_{\text{CH}_2}$  to give two new doubly occupied MOs, the highest of which being an out-of-phase combination which further mixes with the unoccupied  $\pi^*_{\text{CH}_2}$ , in an in-phase way. The resulting highest occupied MO of the system is an orbital in which two hydrogens are combined in an antibonding way to an ethylene  $\pi$ -MO, thus destabilized in the process.<sup>27</sup> Now this interaction is proportional to the square of the overlap between the ethylene occupied  $\pi$ -MO and the  $\pi_{\text{CH}_2}$  and  $\pi^*_{\text{CH}_2}$  orbitals. In structure 4 of BCP, only one ethylene interacts with the CH<sub>2</sub> group, but the ethylene-CH<sub>2</sub> overlap is optimal. On the other hand, in structure 3, two ethylenes interact, so the effect is doubled, but their overlap with the CH<sub>2</sub> orbitals is twice as small as that in structure 4, so the effect is four times smaller. All in all, the influence of the CH<sub>2</sub> group is to destabilize structure 4 twice as much as structure 3. In BCB this effect is much less strong, because two  $\pi_{\text{CH}_2}$  orbitals are now combined to form a bonding and an antibonding MOs. For symmetry reasons, only the first one interacts with the ethylene moiety in structure 3, and the resulting destabilization is weak because the bonding combination of  $\pi_{\text{CH}_2}$  orbitals is lower than that of a single  $\pi_{\text{CH}_2}$ . On the other hand, no symmetry reasons prevent the high-lying antibonding combination of  $\pi_{\text{CH}_2}$  orbitals to interact with two ethylenes in structure 4, which is consequently more destabilized than it is in BCP. For these reasons, the influence of the CH<sub>2</sub> groups on structures 3 and 4 of BCB is nearly balanced.

This repulsion effect between  $\pi_{\text{CH}_2}$  and benzene  $\pi$  electrons also manifests itself in another way, on the two adjacent bonds; the proximity of the CH<sub>2</sub> group to one end of these bonds polarizes their charge density away. This is apparent when one examines the relative weights of structures 5 and 6. This time, the proximity effect should be about the same in BCP and BCB, the exocyclic bond lengths being nearly equal. We indeed find that the 5:6

**Table III.** Structural Weights for Naphthalene, Naphtho[b]cyclopropene, and Naphtho[b]cyclobutene in Their Experimental Geometries and for Distorted Naphthalenes

			
naphthalene	0.197	0.197	0.606
NCP equil geometry	0.265	0.144	0.591
distorted naphthalene (as in NCP)	0.252	0.166	0.582
NCB equil geometry	0.223	0.183	0.594
distorted naphthalene (as in NCB)	0.218	0.192	0.589

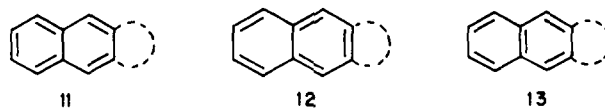
weight ratios are 1.086 and 1.097 in BCP and BCB, respectively, thus confirming our explanation of the MN effect.

#### IV. Extension to Larger Analogues

It now remains to understand the puzzling discrepancy between our results, evidencing a significant MN effect for annelated benzenes, and those of Mitchell et al., concluding to the absence of such an effect in cyclobutane-annelated dihydropyrene. A possible explanation would be that, as we have shown in the preceding section, the influence of a cyclobutane on an aromatic ring is only due to the geometric distortion it exerts at the level of the  $\sigma$  bonds. Such an interaction depends heavily upon the geometry of the non-annelated compound, and it may be of small importance in the case of dihydropyrene. On the other hand, we would predict a sizable MN effect in a cyclopropane-annelated dihydropyrene, because it acts by directly repelling the  $\pi$ -electron cloud, and such an interaction is known to propagate at long distances in conjugated molecules. Thus, if our hypothesis is true, Mitchell's conclusions cannot be generalized to all aromatic hydrocarbons nor to all annelating strained rings.

It is unfortunately impossible to perform a realistic valence bond calculation on annelated dihydropyrene, if only because a reliable geometry optimization would be prohibitively costly for a molecule this size. However, some indications may be provided by naphtho[b]cyclopropene (NCP) and naphtho[b]cyclobutene (NCB), for which experimental geometries are available<sup>7</sup> (see Figure 1). We thus calculated the SCF wave functions of NCP and NCB, using these geometries; then as indicated in section II, we separated the  $\pi$ -MOs of the naphthalene fragment from those of the CH<sub>2</sub> group(s), by using Boys' localization procedure, and performed the VB analysis on the first set of MOs alone. This latter approximation was justified by the marginal participation of structures displaying exocyclic bonds in BCP and BCB, and by the fact that the localized MOs were effectively well separated in NCP and NCB. In addition, to better estimate the consequences of such an approximation, we applied it to BCP and compared the results to those of the complete calculations in section II. Encouragingly, all structural weights were found to be reproduced with an error smaller than 1%. In particular, the ratio of the two Kekulé structures remains unchanged.

The results of the VB analysis of NCP and NCB are summarized in Table III, together with those of naphthalene. It appears that the main features of the naphthalene VB description, i.e., the preponderance of structure 13 over 11 and 12, is not altered by annelation. On the other hand, the relative weights of



structures 11 and 12 are very different in NCP, thus indicating a significant MN effect, while they are much less different in NCB, in agreement with the tentative predictions we formulated above. As there are now three Kekulé structures vs. only two in the case of annelated benzenes, it is not easy to compare the extent of the MN effect in naphthalene derivatives with this of benzene derivatives. One can, however, define a kind of "bond localization index" as the sum of the variations of Kekulé structural weights,

(27) For an analogous effect, see, for example, Hoffmann (Hoffmann, R. J. Am. Chem. Soc. 1968, 90, 1475), where it is shown that such an interaction pushes the symmetrical nonbonding MO over the antisymmetrical one in the trimethylene diradical.

in the way predicted by Mills and Nixon, divided by the sum of all Kekulé structural weights. Thus defined, this index takes the values 0.142, 0.140, 0.106, and 0.019 for BCP, BCB, NCP, and NCB, respectively. It appears from these considerations that the MN effect is drastically reduced from benzene to naphthalene, when the annelating ring is cyclobutane, while it remains significant with a fused cyclopropane.

As in the case of BCP and BCB, we also performed calculations on distorted unannulated naphthalenes, having the geometries of the naphthalene fragments in NCP and NCB. The results, displayed in the third and fifth rows of Table III, indicate that the MN effect due to pure geometrical distortions is very small in NCB, as expected; on the other hand, it looks surprisingly significant in NCP, and this seems to be contrary to our assumption that the effect of geometrical distortions should gradually collapse as the aromatic ring gets bigger. It should however, be noted that the results of the latter calculations can be taken as a measure of the purely geometrical effect of  $\sigma$ -bond distortions, due to the neighboring strained ring, only in the case when the electronic effect of the  $\text{CH}_2$  group(s) on the naphthalene  $\pi$ -MOs is negligible, i.e., in the case of NCB. Otherwise, the distortions of the naphthalene ring can be due, in part, to the MN effect itself, of which they are a secondary consequence rather than a cause. Secondly, the geometric distortions are more favorable to a MN effect in NCP than they are in BCP; the reason for this is that the small ring is attached to a long C-C bond of naphthalene (1.415 vs. 1.364 Å for the neighboring ones, while all are 1.40 Å long in benzene), therefore the shortening of the junction bond in NCP leaves it longer than the two adjacent ones, while the reverse was true in BCP, thus neatly favoring structure 11.

#### V. Conclusion

Our results support the effectiveness of the Mills-Nixon effect as it was originally proposed, i.e., a  $\pi$ -bond-localization effect on strained-ring-annelated benzenes. The geometric distortions of the benzene frame, induced by the strained fused ring at the level

of the  $\sigma$  bonds, are the only cause of the MN effect in BCB, while this factor is less important in BCP where a direct polarization of the  $\pi$ -electron cloud by the  $\text{CH}_2$  group is at least as much effective. As discussed above, it is difficult to quantify the importance of the pure geometrical effect when it is not the only effective factor. Yet, the fact that half the MN effect is already present in BCP with a standard geometry suggests that it is caused, for the most part, by the direct electronic effect of the  $\text{CH}_2$  group.

Our results also indicate that the MN effect is much larger for NCP than it is for NCB, while examination of geometrical distortions alone, with respect to naphthalene, would suggest a smaller difference between these derivatives. These results are coherent with the idea that the effect of a cyclobutane ring is purely locally geometric, and depends strongly on the geometry of the parent molecule, while the polarization of the  $\pi$ -electron cloud induced by a fused cyclopropane ring might still be effective in large systems. The extension to larger annulenes may not be straightforward since naphthalene is a benzo(6)annulene rather than a bridged (10)annulene. However, we can tentatively predict that the  $\pi$ -electron effect of a cyclopropane ring would increase in larger annulenes, as a result of stronger pseudo-Jahn-Teller mixing. On the other hand, the effect of the  $\sigma$  distortion induced by a cyclobutane ring is difficult to predict without any knowledge of the geometries of the annelated as well as non-annelated molecules, and might well vary from one compound to another. Thus, although we find a rather small MN effect in BCB, and Mitchell found almost no effect in cyclobutane-annelated dihydropyrene, it would be unwise to attempt any generalization of these results to cyclobutane-annelated large systems.

**Registry No.** 2b, 95842-00-5; benzocyclopropane, 4646-69-9; tricyclo[4.1.0.0<sup>1,4</sup>]hepta-2,5-diene, 95841-96-6; tricyclo[3.2.0.0<sup>2,4</sup>]hepta-1-(6),3-diene, 95841-97-7; benzocyclobutane, 694-87-1; tricyclo[4.2.0.0<sup>1,4</sup>]octa-2,5-diene, 95841-98-8; tricyclo[4.2.0.0<sup>2,5</sup>]octa-2(5),7-diene, 95841-99-9; naphtho[b]cyclopropane, 286-85-1; naphtho[b]cyclobutene, 6827-31-2.

## A Simple Relation between Nuclear Charges and Potential Surfaces

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**Abstract:** The nuclear charges in a molecular system have a major role in determining most chemical properties. This fact is well recognized; however, this dominant influence of the nuclear charges has not yet been fully exploited in establishing simple rules for polyatomic molecules. In particular, various molecular energy components are often *concave functions* of the nuclear charges. This fact can be used for the derivation of trends in the relative stabilities of different molecules and to prove that an entire potential surface of one molecule lies above that of another molecule. In several recent studies concavity properties of molecular electronic energy functionals have been used to derive various local and global bounds for *electronic energy* hypersurfaces of isoelectronic molecules and chemical reactions. Since the nuclear repulsion energy is *not* in general a concave functional of the nuclear charges, the extension of the above local and global energy constraints to the molecular *total energy* functional (to potential energy surfaces) has met with difficulties. In the present study a simple sufficient and necessary criterion is given for the existence and for the evaluation of such constraints for total energy functionals. These constraints lead to rules for the energy ordering of different chemical species and to an ordering of potential energy surfaces. The applications of these rules require only a simple inspection of the nuclear charges and elementary calculations on a pocket calculator. Several examples are given.

Molecular properties and chemical reactions are fundamentally influenced by the magnitude of nuclear charges present in a given chemical system. In a formal sense the molecular total energy may be regarded as a function  $E(\mathbf{z}, \mathbf{r})$  of both the nuclear charges  $\mathbf{z}$  and the nuclear geometry  $\mathbf{r}$ , where  $\mathbf{z}$  is a formal vector variable

containing the nuclear charges as components, whereas vector  $\mathbf{r}$  represents the collection of internal coordinates for the molecule. Within this model one may obtain energy relations between two molecules by analyzing the dependence of this function on variables  $\mathbf{z}$  and  $\mathbf{r}$ , as they change their values from  $\mathbf{z}(1)$  and  $\mathbf{r}(1)$  of molecule