Effects of strain and conjugation on the structure of the benzene ring in a free benzene molecule, in benzofuran, 1-indanone, and phthalide

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MNDO calculations show that the alternation of bond lengths which is observed in a benzene ring, when there is a five-membered aliphatic fused ring (Mills—Nixon effect) as well as a heterocyclic one, is induced by the only lengthening of the bridgehead bond under the strain of the fused ring, and no other specific effect is to be involved. Such an alternation is a basic feature of the benzene ring when one of its bonds is lengthened. When alternation occurs, since the hexatriene structure is the model structure which should be reached for a bond infinitely lengthened, it is rather an open chain hexatriene-like structure which tends to be reached instead of a Kekulé-like one.

We show that a weak conjugation does not prevent the alternation of bond lengths to occur under the strain of the five-membered fused ring, since it is observed in 1-indanone. When conjugation is more effective, involving the whole five-membered ring, as in benzofuran, conjugation tends to impose an alternation opposite to that induced by the strain of the same fused ring, and, as concerns the bond lengths, blurs the structural incidence of the Mills—Nixon effect. The opposition is the strongest in the region of the bridgehead bond where the strain is the most efficient. Conjugation is efficient through extended system, and it is stronger to impose its own alternation pattern inside the benzene moiety (apart the bridgehead bond) where the effect of the strain is rapidly decreasing. When using the π bond orders, the alternation pattern imposed by the conjugation with the five-membered ring is more clearly set up, since the bond orders are more typical of the conjugative process, and the new alternation pattern is no more a Mills—Nixon effect.

Our work has been extended to phthalide to ascertain the generality of the alternation pattern under strain.

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Расчеты методом MNDO показывают, что колебание длин связей, наблюдаемое в бензольном кольце при наличии сопряженного пятичленного алифатического цикла (эффект Миллза—Никсона), а также гетероциклического кольца, вызывается только удлинением связи, находящейся в голове моста, под воздействием напряжения сопряженного цикла, причем никакой другой специфический эффект не имеет места. Такое колебание является основной характеристикой бензольного цикла при удлинении одной из его связей. При наличии колебания, поскольку гексатриеновая структура является модельной, к которой стремится соединение при бесконечном удлинении связи, молекула стремится приобрести вид открытой цепи с гексатриеновой структурой, а не кекулевской структурой.

Нами показано, что слабое сопряжение не препятствует протеканию колебания длин связей под действием напряжения пятичленного сопряженного кольца, поскольку оно наблюдается в 1-инданоне. При более эффективном сопряжении, включающем все пятичленное кольцо, как в бензофуране, сопряжение ведет к появлению колебаний, противоположных к вызываемым напряжением того же сопряженного кольца, и, что касается длин связей, приводит к нарушению структурных последствий эффекта Миллза—Никсона. Это противоположное действие наиболее сильно в близости связи в голове моста, где напряжение наиболее действенно. Сопряжение действует через расширенную систему и вызывает характерные колебания наиболее сильно внутри бензольной части (вдали от связи в голове моста), где влияние напряжения быстро падает. При использовании порядков π связей вид колебания, вызываемый сопряжением с пятичленным кольцом более явно выражен, поскольку порядки связей более типичны для процесса сопряжения, и новый вид колебания более не является следствием эффекта Миллза—Никсона.

Наша работа была расширена на случай фталида с целью доказательства общезначимости вида колебаний, вызываемых напряжением.

In preceding papers [1, 2] we have shown that the Mills—Nixon effect, considered from a structural point of view, is not restricted to benzocycloalkenes such as indane. This effect leads, in benzodioxole (benzodioxolane), (Fig. 1) to an alternation of bond lengths towards what is sometimes named a "Kekulé structure". Actually, it has been assumed in the same works that the alternation of bond lengths could arise from the only lengthening of the bridgehead bond, belonging to the benzene moiety and to the five-membered fused ring. If a bond in a benzene ring was lengthened "infinitely", the molecule should be distorted towards a "linear" hexatriene-like structure with bond lengths alternation, as it occurs in hexatriene itself. It has been assumed on such a ground, and on the basis of steric effects considerations, that it would be easier to observe the alternation, when the lengthening of a bond is induced by a

five-membered ring rather than by two *ortho* noncyclic substituents. In order to establish the above hypothesis on a firmer theoretical basis, we are going to study in this paper the incidence of lengthening or contracting one of the bonds, on the structure of a free benzene molecule, placing our work in the more general field of studies on structural properties of conjugated systems, the
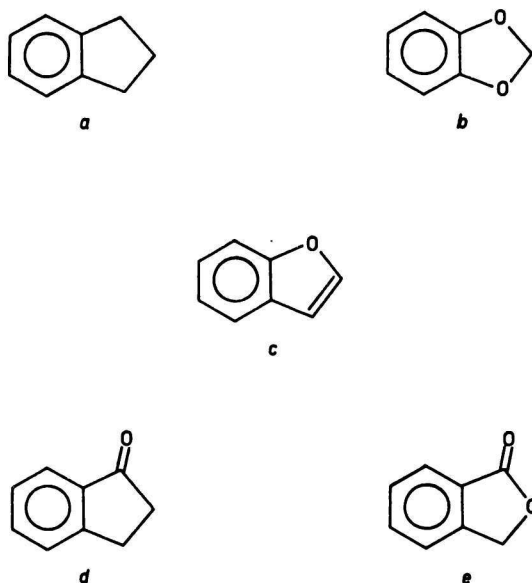

Fig. 1. a) Indane; *b)* benzodioxole (benzodioxolane); *c)* benzofuran; *d)* 1-indanone; *e)* phthalide.

classical picture of which has been recently reinvestigated [3—10]. Furthermore, such a study — which is extended to benzofuran, 1-indanone, and phthalide (Fig. 1) — is a step to understand the structural driving forces which impose their geometry to the molecules containing benzene moieties with five-membered fused rings. These molecules are common (with or without heteroatoms or conjugated bonds) in natural products. They constitute one of the interests of our laboratory for their antifungal potentialities when they bear oxygen atoms.

I. Distortion of a free benzene molecule

Our present MNDO calculations show that, when the length of the bond *a* (Fig. 2) is increased, the double bond character increases in bonds *b, d, f* (they contract and their π bond orders increase) and the single bond character

increases in bonds *a*, *c*, *e* (Table 1). Thus, there is a definite tendency towards an alternation of bond lengths as well as an alternation of π bond orders, since bond orders and bond lengths are linked.
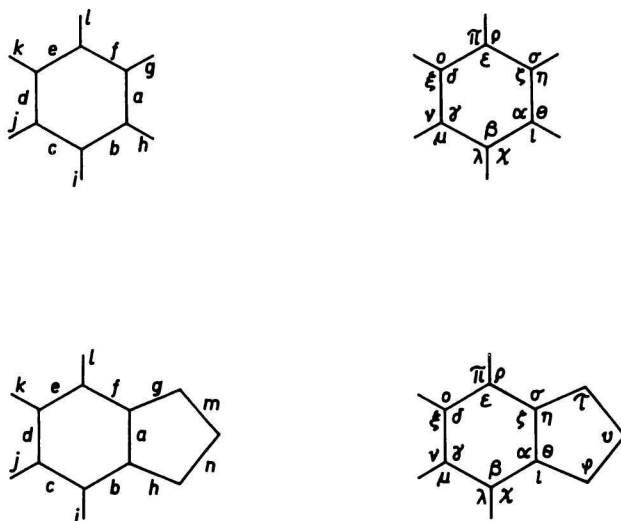

Fig. 2. Denotation of bonds (Latin letters) and angles (Greek letters).

In the present calculation there is no five-membered fused ring; we have introduced an "arbitrary" lengthening of one of the bonds (the bond *a*) and the alternation is still observed. Consequently, when there is a five-membered ring, the alternation is induced by the lengthening of the bridgehead bond under the "mechanical" strain of that ring. There is no need to assume some specific effect from the fused ring to explain the alternation. Of course, the fused ring could induce specific effects (conjugation, σ and/or π electronic effects from heteroatoms, *etc.*) which could interfere. Nevertheless, it is the lengthening of the bridgehead bond which, by itself, is the basic phenomenon, the cause of the alternation.

Another point is worthy of notice. When the bond *a* is distorted to 1.54 Å — which is the length of a pure classical C—C bond — we do not reach a Kekulé structure. That is to say a structure with alternating pure double and pure single bonds. The elongated bond *a*, still displays a high degree of double bond since its π bond order is still 0.50, when it is 0.67 for a bond in the nonperturbed benzene molecule. The conjugation inside the ring is not destroyed by the lengthening. The bonds *c* and *e* should be single bonds in a Kekulé structure.

Table 1

Bond lengths (Å) in a distorted benzene molecule

a	b	c	d	e	f
1.330	1.428	1.394	1.391	1.391	1.430
1.360	1.420	1.398	1.417	1.398	1.421
1.390	1.411	1.404	1.404	1.404	1.412
1.420	1.404	1.410	1.405	1.410	1.404
1.450	1.395	1.417	1.398	1.416	1.395
1.480	1.388	1.422	1.394	1.420	1.389
1.510	1.381	1.427	1.389	1.426	1.382
1.540	1.378	1.430	1.385	1.429	1.378

The bonds b, c, d (and e, f which are respectively equal to c and d) have been optimized for a given bond length a. C—H bond length has been kept 1.084 Å.

Bond orders in a distorted benzene molecule for different values of the bond lengths a (the left column)

a/Å	a	b	c	d	e	f
1.330	0.762	0.566	0.750	0.580	0.751	0.565
1.360	0.729	0.603	0.721	0.612	0.721	0.603
1.390	0.689	0.645	0.686	0.648	0.686	0.645
1.420	0.649	0.683	0.651	0.681	0.651	0.683
1.450	0.605	0.722	0.613	0.715	0.614	0.722
1.480	0.567	0.753	0.581	0.741	0.582	0.753
1.510	0.528	0.782	0.549	0.767	0.550	0.782
1.540	0.497	0.803	0.525	0.785	0.525	0.803

Bond angles (°) in a distorted benzene molecule

a/Å	α	β	γ	Θ	χ	μ
1.330	120.7	119.7	119.5	121.5	119.4	120.9
1.360	120.3	120.2	119.8	121.0	119.4	120.7
1.390	120.1	120.1	118.8	120.4	119.9	120.2
1.420	119.9	120.0	120.1	119.7	120.1	119.9
1.450	119.6	120.1	120.3	119.1	120.4	119.4
1.480	119.3	120.2	120.5	118.6	120.5	119.2
1.510	119.0	120.2	120.8	118.0	120.7	118.9
1.540	118.1	120.4	121.0	117.6	120.7	118.7

The values for symmetric parameters are given only once.

Their π bond order is still 0.53, higher than the π bond order of a: the incidence of the perturbation weakens with distance. The benzene ring "buffers" the distortion from a $\mathbf{D}_{6h}$ symmetry.

The fact that, when lengthening a bond, we observe an alternation of bond lengths, cannot be taken as a proof that a Kekulé structure should be the "natural" structure of the π system of benzene, when that system is taken alone, as it has been assumed several times recently [3, 5—8]. It is no more a proof against, since in our work the σ frame is conserved. We want to take into account π and σ electrons since, here, the separation of π electrons from the core, in the field of which they are moving, should be artificial: the elongation of the bond a involves the σ frame, as well as the π cloud. Nevertheless, although our interest is slightly different from the works cited above on the Kekulé structure, our present results emphasize also the alternation of the bond lengths, alternation which is hidden inside the $\mathbf{D}_{6h}$ symmetry, and which is able to appear at the least perturbation lengthening or contracting one of the bonds.

Our MNDO calculations which show that it is very difficult — if not impossible — to reach a Kekulé structure when lengthening a bond, show as well that such a structure cannot be reached by contracting one. The contraction of the bond a induces a smaller effect towards an alternation than the lengthening does. Actually, the contraction of a increases the crowding of the molecule on a smaller space, since it decreases the average bond length. Its lengthening induces the opposite effect. The distorted bond shifts the average bond length towards its own distortion. For example, the perimeter is 8.540 Å length when the bond a is 1.540 Å, and it is only 8.363 Å length when the bond a is 1.33 Å. Such a contraction of the whole molecule prevents the elongated bonds to become as long as those observed when a is lengthened.

Furthermore, it is worthy of notice that inside the ring, the lengthening of a closes the angles α and ζ and opens β, ε, γ and δ. This is linked to a sort of mechanical behaviour of the bonds under the strain opening the ring: the whole molecule opens (Fig. 3). When contracting the bond a the reverse should be observed. Actually, the angles Θ and η increase (Table 1), χ and ϱ decrease slightly. Inside the ring, α and ζ open when the other angles close. The amplitude of the phenomenon is less marked than the precedent ones, since the whole process of the alternation itself is less marked.

Fig. 3. Incidence, on the angles of the benzene molecule, of the lengthening (left part of the figure) or the contracting (right part of the figure) of the bond a.

One should note too, that in the "Kekulé" structure, when using alternating 1.54 Å and 1.33 Å bond lengths, the calculation shows that these bond lengths do not correspond to pure single and pure double bonds. The π bond order for 1.54 Å is 0.90, it is 0.35 for 1.33 Å. It should be necessary to much more extend the elongated bonds and much more contract the others to localize the bonds. That result parallels what is observed when lengthening the bond a alone, when the ring "buffers" the destruction of conjugation.

When lengthening a bond in a free benzene molecule, the angles behaviour is different from what is observed when there is a five-membered fused ring. We have shown [2] that when the fused ring lengthens the bridgehead bond (say a), the angles Θ and η decrease to release the strain, since these angles are part of the fused ring, and the whole benzene moiety contracts slightly: the distance between d and a decreases. Actually when there is a fused ring, the angle α is led to increase, because ι increases to follow the decrease of Θ. On the contrary in the "free" benzene molecule — when the bond a is lengthened — bond lengths and bond angles optimize without the strain of the fused ring: Θ and η are no more forced to decrease because of that strain; they decrease because of the decrease of the repulsion between the C—H bonds g and h.

Furthermore, the scheme in the "free" benzene molecule is different from what arises in an *ortho* disubstituted molecule without fused ring, as it has been studied in a preceding work [2]. We should notice that the alternation of bond length in the distorted benzene molecule reaches a hexatriene-like pattern rather than a Kekulé-like one. Actually, when we weaken the conjugation across one of the bonds in the free benzene molecule, by perturbing that bond only, the rest of the molecule optimizes with the effect of the perturbation decreasing with the distance. Destroying completely the conjugation in one of the bonds should be similar to "cut" that bond as concerns the π system, and we should be in the case of an open hexatriene-like molecule. To reach a Kekulé structure we should have to destroy the conjugation of three bonds at the same time.

Another point which is worthy of notice is the decrease of the ionization potential when lengthening as well as contracting a bond in the "free" benzene molecule (contracting is far less efficient than lengthening) (Table 2). Actually, the energy of the π HOMO increases when the strain is stronger, and the energy

Table 2

Energy of the HOMO for the different values of the bond lengths a of the benzene molecule

$a/$Å	1.330	1.360	1.390	1.420	1.450	1.480	1.510	1.540
$E/$eV	−9.3405	−9.3541	−9.3756	−9.3607	−9.3055	−9.2518	−9.2123	−9.1705

of the virtual π SCF LUMO decreases. This π SCF LUMO which is virtual "stricto sensu", is analogous in this work, for the free benzene molecule (where there is separation between σ and π system) to the π Hückel LUMO (considering the free nondistorted $\mathbf{D}_{6h}$ benzene molecule, the π SCF MNDO MO are the same as π Hückel MO and are imposed by symmetry). Such a decrease of the LUMO should favour antifungal properties [11]. Actually, in pterocarpin one of the two benzene rings is fused with two five-membered oxygenated rings, and this natural product is known with many of its derivatives for its antifungal properties.

II. Alternation of bond lengths in some molecules containing a five-membered ring fused to a benzene moiety: benzofuran, 1-indanone and phthalide

In our preceding works [1, 2], we have shown that there is a strong alternation of bond lengths in benzodioxole although there is a strong coupling between the oxygen atoms and the π system. Considering these results we could be led to assume that strong electronic effects do not prevent the alternation of bond lengths to occur. In fact, although the nonbonding orbitals of the oxygen atoms in benzodioxole are coupled to the π system, this molecule is not a classical example of conjugation. In order to see if some alternation of bond lengths still exists when the π system is lengthened outside of the benzene moiety we have studied the benzofuran, 1-indanone, and phthalide molecules (Fig. 1).

A. Strain and conjugation effects in the benzofuran molecule

This molecule is less symmetric (symmetry $\mathbf{C}_s$ instead of $\mathbf{C}_{2v}$) than indane and benzodioxole. Furthermore, conjugation extends all around the molecule when taking into account the coupling of the "nonbonding" orbitals of the oxygen atom with the π system. The alternation of bond lengths is no more observed (Table 3). The π system contains 6.121 electrons, which is lower than what has been observed in benzodioxole (6.149) since there is only one oxygen the π donating ability of which splits up towards two directions. Nevertheless, the π system is more extended than what occurs in benzodioxole and there is no break of continuity inside the five-membered ring.

Although there is no obvious alternation of bond lengths in the benzene ring, there is still an increase of the bridgehead bond (1.441 Å) (compared to the benzene molecule (1.397 Å)) as occurs in indane (1.428 Å) and in benzodioxole (1.439 Å). There is also a strong alternation among the π bond orders. This would be quite surprising considering a "free" π system, since an increase of

Table 3

MNDO geometry of benzofuran

Bond	a	b	c	d	e	f	g	h	m	n
Length /Å	1.441	1.410	1.400	1.421	1.401	1.413	1.372	1.455	1.375	1.383
Order	0.610	0.583	0.726	0.602	0.723	0.586	0.363	0.401	0.377	0.868

The C—H bonds have been taken 1.084 Å length. The oxygen atom is between the bonds g and m (see Fig. 2).

Species	α	β	γ	δ	ε	ζ	η	Θ
Angle /°	118.9	118.8	121.2	121.7	116.5	122.6	110.2	104.7

Species	χ	μ	ξ	π	τ	ν	φ
Angle /°	120.5	119.8	118.7	121.6	106.9	112.0	106.2

The bond angle H—C-12—C-4 is 127.4°; the bond angle H-14—C-13—O-11 is 126.1° (the numbering of the atoms is given in Fig. 5).

bond orders would parallel an increase of the strength of the bonds and a decrease of the bond length. Here, the π system is superimposed to a σ frame and the lengths of the bonds depend strongly on that frame. When considering the five-membered ring the π bond order of the bond n (the double bond) is 0.868. It is lower than 1 because of the conjugation which causes an electron migration towards the neighbouring bonds. The bond n displays a π-character higher than what is observed for a bond in the benzene moiety. This will impose an alternation of π bond order inside the five-membered ring in the part of that ring where the π system is the most concentrated, the most developed; that is to say in the part n—h—a. The result should be an increase of the π bond order of the bond a, in so far as that bond can pass to belong to the five-membered ring. This is well known *e.g.* for butadiene or for cyclopentadiene, where the π bond order is lower for the bond which is between the two "formal" double bonds. Thus, the only existence of the double bond n should cause an increase of the π bond order in the bond a in order to reach the most stable distribution of π electrons in the five-membered ring. That effect would be alone, the length of the bond a should decrease.

As occurs in indane and benzodioxole the length of the bond a should increase because of the "mechanical" strain of the five-membered fused ring. That lengthening should decrease the π bond order of the bond a (indane: 0.62; benzodioxole: 0.56) from what is observed in a free benzene molecule (0.67). Thus, conjugation and strain have opposite effects on the length of the bond a. Our calculations show that conjugation is not sufficient to prevent the lengthening of that bond under the strain of the five-membered ring, although it tends to increase the π bond order favouring a decrease of its length.

As it has been observed in indane and benzodioxole the only lengthening of the bond a should lead to alternating bond lengths: b, d, f being shorter than a, c, e. Consequently, the π bond order should be lower for these latter bonds.

On the contrary, the conjugation effects induced by the five-membered ring which tends to increase the π bond order of the bond a, should increase also the π bond order of c and e. They should decrease those corresponding to the bonds b, d, and f, the lengths of which would be increased compared to a, c, e. What is observed is the result of these two opposite effects.

At first glance, the alternation of π bond orders in the benzene moiety could appear as roughly independent of the bond lengths (Table 3). In fact, the behaviour of the bond a, region where the two opposite effects are the most conflictuous, prevents the alternation of bond lengths to be observed. Actually, when that bond is not taken into account, the bond lengths b, c, d, e, f are respectively: 1.410, 1.399, 1.421, 1.401, 1.413 Å. There is alternation, but the order of this alternation is just the contrary to what happens in indane and benzodioxole. The bonds b, d, f, are the longest bonds in benzofuran; they are

the shortest ones in indane and benzodioxole. Furthermore, the longest bonds *b*, *d*, *f* display the lowest π bond orders, which is what is to be expected when the π bond order of *a* increases. That is to say: the conjugation of the five--membered ring imposes the alternation pattern inside the benzene moiety. The main effect induced by the strain of the five-membered ring is the increase of the length of *a*. The effect of conjugation extends to farther parts of the molecule than the strain does.

B. Strain and conjugative effects in the 1-indanone molecule

In the 1-indanone molecule (Table 4), the conjugative pattern is different from the preceding one: the fused ring does not take part as a whole in the conjugated system. There should be a lower perturbation on Φ than in the previous case.

The π bond order between CO and Φ (bond *g*) is 0.217, higher than what has been observed for the same bond in indane (0.145) where there is only a hyperconjugative interaction, lower than what appears in benzodioxole (0.269) and, of course, much lower than what appears in benzofuran (0.401 for the bond *h*, and 0.363 for the bond *g*). The total π electron density is 5.971, when it is 6.011 for indane, 6.149 for benzodioxole and 6.121 for benzofuran. Such a low value for 1-indanone arises from the π electron withdrawing character of the C=O bond. Although the perturbation of the π_Φ system could seem lower than what is observed in benzodioxole — since the total π_Φ electron density is nearer to 6 — there is nevertheless a classical conjugation. Our calculations show that such a conjugation does not destroy the alternation of bond lengths inside the benzene ring (conjugation involves only a part of the substituents). The driving force to distort the structure is no more conjugation but strain. Bond alternation in the benzene moiety is to be compared to what happens in indane and benzodioxole.

In 1-indanone, the part of the five-membered ring which is external to the benzene moiety is of 6.179 Å length. That length is 6.119 Å for indane and 5.592 Å for benzodioxole. The five-membered ring should all the more lengthen the bridgehead bond the shorter is its own length outside the benzene ring [2]. The strain on that bond would be stronger. Actually, in benzodioxole, the bridge-head bond is of 1.439 Å length, in indane of 1.428 Å and in 1-indanone of 1.421 Å. The strain would be the only interaction between Φ and the five-membered ring, we should observe a greater alternation when the bridgehead bond is longer.

We have already defined an alternation index [2]. In order to extend that index to π bond order, we slightly modify its definition

Table 4

MNDO geometry of 1-indanone

Bond	*a*	*b*	*c*	*d*	*e*	*f*	*g*	*h*	*m*	*n*
Length /Å	1.424	1.400	1.416	1.403	1.415	1.400	1.497	1.514	1.542	1.584
π order	0.606	0.695	0.635	0.692	0.639	0.680	0.217	0.000	0.000	0.000

The C—H bonds have been taken 1.084 Å length and the CH—H bonds 1.107 Å. The C=O bond involves the carbon atom between the bonds *g* and *m*.

Species	α	β	γ	δ	ε	ζ	η	Θ
Angle /°	120.9	118.9	120.1	121.0	119.0	120.0	109.6	113.1

Species	χ	μ	ξ	π	τ	ν	φ
Angle /°	121.2	119.7	119.7	119.8	106.8	107.5	101.7

The dihedral angle involving the atoms 14, 12, 4, 3 is 118.8°; that involving 15, 12, 4, 3 is 241.2°; that involving 17, 13, 11, 3 is 120.2°; that involving 16, 13, 11, 3 is 239.7° (the numbering of the atoms is given in Fig. 6).

B. VIDAL, J. VARDIN, A. DARRY-HENAUT

$$A_L = 100(L - l)/L \text{ and } A_\pi = 100(\Pi - \pi_1)/\Pi$$

L is the average of the three longest alternating bond lengths and l the average of the shortest alternating ones in the benzene moiety. Π is the average of the greatest π_Φ bond orders and π_1 the average of the smallest ones. These indices are only defined if there is alternation of bond lengths. The index A_L, measuring the alternation of the bond lengths, is 1.23 for 1-indanone. It is also 1.23 for indane and 2.04 for benzodioxole. For a pure Kekulé structure: $A_L = 100(1.54 - 1.33)/1.54 = 13.64$. In benzofuran, when not taking into account the bond a — which displays a special behaviour — the index A_L is 1.03. This value is weaker than the preceding ones, but we should keep in mind that such an alternation is imposed by the strong conjugation with the five-membered ring against the alternation pattern arising from the strain.

When using A_π for a pure Kekulé structure with alternating single and double bonds $A_\pi = 100(1 - 0)/1 = 100$. We obtain for indane 8.88, for benzodioxole 14.92, for 1-indanone 8.99, and 13.98 for benzofuran. In this latter case the bond a has also been used: when considering the π bond orders and as concerns the alternation pattern, that molecule does not display a specific behaviour. When not considering the bond a, A_π for benzofuran is: $A'_\pi = 18.5$. The value is lower in the first case because the strain on bond a is stronger than conjugation, and opposes to the increase of the π bond order.

Whatever A_π or A'_π is used to evaluate the alternation pattern, that alternation is strongly marked in benzofuran. Conjugation is as much efficient to induce π bond orders alternation in benzofuran as strain in benzodioxole. Thus, in benzodioxole the driving force being the strain, the main effect of the oxygens is not their conjugation with π_Φ (they cannot induce an alternation by the coupling of their "nonbonding" orbitals since alternation needs conjugated double bonds) but the fact that the bonds C_Φ—O are very short (1.369 Å), which imposes a short five-membered ring and a great strain on the bond a.

When the length of the five-membered ring is decreased, increasing the length of the bond a because of the strain, the distance between bonds a and d should decrease as it has been observed in indane and benzodioxole. The angles β and ε should decrease, γ, δ should increase from 120°, α and ζ also. Such a phenomenon has been explained on the only ground of the strain imposed by the five-membered ring on the benzene moiety. The same is observed when comparing 1-indanone with benzofuran (see tables) and with the two preceding molecules.

C. The phthalide molecule

Our preceding works and the above results show that the Mills—Nixon effect — as concerns the structural point of view — should arise every time when a

bond in a benzene moiety is lengthened. Nevertheless, quenching effects, or a too strong conjugation, can prevent to observe clearly the alternation pattern. To ascertain the generality of the alternation pattern under strain we have performed limited optimizations on phthalide. Conjugation is slightly less efficient than in 1-indanone since the π bond order involving C_ϕ—CO is 0.203 when it is 0.217 in 1-indanone. Consequently, our calculations (Table 5) show an alternation of bond lengths to be stronger than in 1-indanone: $A_L = 1.28$ (1-indanone: 1.23), $A_\pi = 9.80$ (1-indanone: 8.99). The coupling of C=O with π_ϕ is lower in phthalide because of the oxygen atom of the lactone which tends to stabilize the π electrons of C=O, in the —CO_2— group. The bond lengths a, b, c, d, e, f, within the Φ moiety (f and e being on the side of C=O) are 1.426, 1.396, 1.416, 1.406, 1.412, and 1.396 Å.

III. Geometric models

The size of the molecular systems under examination, the number of the calculations to perform in order to reach significant results, have led us to use the MNDO method. That method has been preferred also because it gives results which are consistent with what is obtained when using *ab initio* methods on the benzene molecule [9]. For example, *ab initio* methods lead to alternating bond lengths when the lengths of the three bonds a, e, c are given (Fig. 2) the same fixed value. This limits the molecule to a $\mathbf{D}_{3h}$ structure. Our works destroy the symmetry further towards $\mathbf{C}_{2v}$, optimizing not only the bond lengths for a given perturbation but also all the angles inside the ring, and the angles C_ϕ—C_ϕ—H outside the ring. Our results are consistent with the *ab initio* works of *Shaik* [4] and *Epiotis* [3] on benzene for the part where they can be compared.

Our choice has taken into account the fact that the molecules under study are neutral species, since, sometimes, for charged species the MNDO method fails. For example, the intensity of the secondary transition of the chromophore Φ in species $\Phi(CH_2)_n CO_2^-$ decreases when calculations based on the MNDO method show that it should increase [12]. Furthermore, the MNDO method correctly predicts geometries for molecules of the size of those studied in that work. Above all, that method does not emphasize the alternation of bond lengths. Actually, it leads to no alternation at all in the catechol molecule when X-ray experiments show a very small bond alternation [13, 14].

Furthermore, we should keep in mind that *ab initio* methods sometimes fail also when a basis not large enough is taken for the description of atomic orbitals. Moreover, one of us has given one of the first examples of a failure of an *ab initio* method to be consistent with the Koopmans' theorem [15].

Table 5

MNDO geometry of phthalide

Bond	a	b	c	d	e	f	g	h	m	n
Length/Å	1.426	1.396	1.416	1.406	1.412	1.396	1.499	1.525	1.381	1.460
π order	0.603	0.699	0.632	0.693	0.638	0.684	0.203	0.141	0.358	0.161

The C—H bonds have been taken 1.084 Å length and the CH—H bonds 1.107 Å. The C=O bond involves the carbon atom between the bonds g and m.

Species	α	β	γ	δ	ε	ζ	η	Θ
Angle/°	119.9	118.8	120.9	120.6	118.2	121.6	106.9	107.3

Species	χ	μ	ξ	π	τ	v	φ
Angle/°	120.0	120.0	119.8	121.9	108.2	111.8	105.8

The C—H bond angle with the benzene moiety has not been optimized. The calculation has been done with $\chi = \mu = \xi = \varrho = 120°$.

The MNDO method does not allow to optimize in a single calculation an indefinite number of parameter. So we have been obliged for benzofuran and 1-indanone to carry out the optimization in successive steps. The first group of parameters has been optimized — as it is described below —, then with the values obtained for these parameters the second group has been otimized, then with the new values the third one if necessary, *etc.* The whole process has been performed again, optimizing the first group with the new values for the others, then the second one, *etc.* till consistency is obtained for the geometry. Furthermore, our choice of parameters to be optimized and their order has been carried out in order to obtain the best results as concerns angles and bond lengths within the benzene ring.

A. MNDO calculations on the distortion of a free benzene ring

The C—H bonds of benzene were assumed to be of length 1.084 Å. The numbering of the atoms has been that of Fig. 4. To ensure a degree of freedom for calculation there is one of the C—C bonds in benzene for which no input length is given in the MNDO method. This is the bond c between the atoms 2 and 7. When lengthening or contracting the bond a after optimization, the bonds c and e should have the same length. This behaviour has been used as a criterion to avoid artefacts. When no input data were given for the bond d, instead of the bond c, a symmetry was introduced in calculations and it was impossible to compare d to another bond in order to check the reliability of the calculations. Precisely, there was obviously an artefact. The bond length d increased with the bond order. When taking the above numbering there was no difficulty.
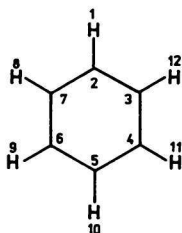

Fig. 4. Numbering of the atoms in a benzene ring.

B. MNDO calculations on benzofuran

The C—H bond lengths (they are C_π—H bonds) have been kept constant with the value 1.084 Å. In the first calculation, the following parameters have

618

been optimized: all the other bond lengths (the C=C bond length excepted), the angles, except those determining the position of H-9, H-10, O-11 with the rest of the molecule (Fig. 5). In the second calculation, using the above optimized value, these parameters were optimized: all the bond lengths, all the angles, the bond lengths C_π—H, O-11—C-3, C-12—C-4, O-11—C-13 excepted. Thus, a few parameters only have been optimized once; angles and bond lengths inside the benzene ring have been optimized twice. The second optimization introduces only very small changes in the benzene parameters. One point is worthy of notice: alternation is not sensitive to the angles of C—H bonds with the benzene moiety, provided these angles are kept around 120°.
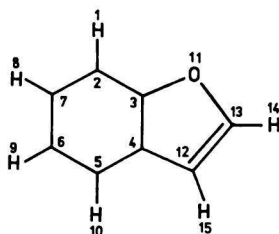

Fig. 5. Numbering of the atoms in the benzofuran molecule.

C. MNDO calculations on 1-indanone

The C=O bond length has been optimized separately obtaining 1.221 Å, with a standard geometry for the molecule. In the first calculation the C—H bond lengths have been kept constant using the values 1.084 Å for C—H and 1.107 Å for CH—H. All the other bond lengths, all the angles inside the benzene ring, the angles (Fig. 6) O=C—C_Φ (127.1°), CH$_2$—CO—C_Φ (τ = 106.8°), OC—C_Φ= =C_Φ (η = 109.6°), C_Φ—C_Φ—CH$_2$ (Θ = 113.1°), C_Φ—CH$_2$—CH$_2$ (φ = 101.7°) (internal to the five-membered fused ring) were optimized.
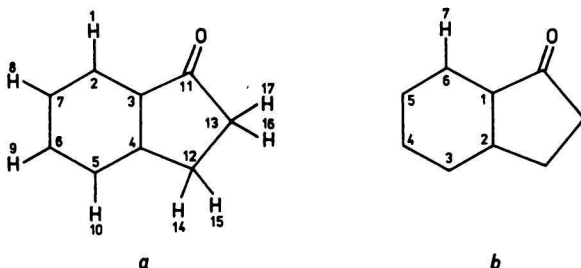

Fig. 6. The two numberings used for the atoms in the 1-indanone molecule in order to check the reliability of the calculations.

In the second calculation, all the angles involving the C—H bonds (those involving the bonds j and k excepted), comprising the dihedral angles involving the C—H aliphatic bonds in the five-membered ring were optimized.

In the third calculation, the C—H bond lengths have been optimized separately. The result is: 1.090 Å for C_Φ—H and 1.109 Å for alkyl C—H. These values are near to the standard values (1.084 and 1.107 Å).

In the fourth calculation, using the above optimized parameters the numbering of the atoms has been changed. We wanted to be sure that the alternation pattern is not an artefact which occurs from the numbering order used to carry out the calculation. In the above calculations we used the numbering shown in Fig. 6a, the new calculation used the numbering of Fig. 6b. The bond lengths and bond angles within the benzene moiety, the angles of H—C_Φ with benzene and the angles O=C—C_Φ, CH_2—CO—$C_\Phi(\tau)$, OC—C_Φ—$C_\Phi(\eta)$, C_Φ—C_Φ—CH_2 (Θ), C_Φ—CH_2—$CH_2(\varphi)$ were optimized. The geometry obtained is not sensitive to the numbering used.

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