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Comparison of potential energy maps and molecular shape invariance maps for two-dimensional conformational problems

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Summary. It is well known that many molecular properties are strongly dependent on internal nuclear arrangements. Two possible, independent approaches can be followed while studying changes in molecular characteristics as functions of the nuclear geometry. These are the analysis of potential energy surfaces and the analysis of molecular shape. In this work, we seek to establish relationships between potential energy maps and shape invariance region maps, where each point of these maps represents a nuclear configuration. The study is performed by analyzing the occurrence and lack of certain symmetries in both types of maps. As illustrative examples, we consider the three structural isomers of the dihydroxybenzene molecule. Potential energy is computed at the STO-3G *ab initio* level, while the shape is described by the shape group method as applied to fused-sphere van der Waals surfaces. It is shown that the symmetry of the shape invariance maps follows closely, but not exactly, the symmetry of potential energy surfaces. The molecular surface is thus "blind" to some small changes of the potential (a feature to be expected to hold also for molecular surfaces defined in terms of electronic charge density). Our findings suggest that a crude fused-sphere model may suffice to describe some of the structural changes in molecular surfaces, as well as their relationships to the electronic energy.

Key words: Molecular shape — Conformational energy maps — Shape invariance maps — van der Waals surfaces

1. Introduction

When one considers the influence of certain conformational rearrangements (e.g., internal bond rotations) on molecular properties, it is observed that there are certain ranges of such motions where no major change in the molecular properties occur. Accordingly, a chemical conformer is not a given arrangement of nuclei, but a *continuum* of nuclear geometries. The extent of such a range of continua of geometries may have various definitions. Two of them will be discussed and compared in this article: definition of such ranges in terms of curvature domains of potential energy functions, and in terms of molecular shape invariance domains.

The characterization of relaxed conformational cross-sections of potential energy surfaces of polyatomic systems has been the subject of several studies (see, e.g., [1] and references quoted therein). Applying a general description of potential energy hypersurfaces [2], it is possible to define domains in configuration space from the curvature properties of such surfaces that correspond to the "conformers". A stable conformer will identify a domain in configuration space spanned by the catchment region of conformational paths ending at a specified minimum of the energy hypersurface. This implies a topological definition of the notion of "chemical species" based on potential energy [2].

On the other hand, it is known that certain intermolecular interactions seem to be not only dependent on the energy content, but on some three-dimensional characteristics of a molecule, such as the size and shape of a molecular surface, e.g., an electronic isodensity contour surface [3]. This is the case, for instance, in drug-receptor interactions, often described by models of lock-and-key and hand-in-glove type [4].

Energy content and molecular shape should be dealt with as conceptually distinct notions. In this work we seek to establish some relationships between these two different concepts. The notion of molecular shape may be approached in various ways. Among the possible descriptions we can mention two approaches: a representation by means of points in space corresponding to the atomic nuclei and lines corresponding to the covalent bonds, and another one, using surfaces in 3-space, mimicking the envelope of a three-dimensional molecular "body". The first approach is usually phrased in the context of molecular graph theory, which has been found helpful in rationalizing some aspects of the physical process of intermolecular recognition [5, 6]. However, this approach is not well adapted to describe the relation between shape and molecular conformation, since the usual graph-theoretical descriptions are indeed conformationally invariant. (A notable exception is found in [7]). The alternative method, the use of molecular surfaces, allows one to describe shape changes due to conformational changes in a natural way. In this work we use a topological characterization of model molecular surfaces, the so-called shape group method (SGM [8–10], which is suitable for describing shape invariance along configurational paths [11–13].

We shall consider two-dimensional conformational subsets of internal coordinates in order to analyze the relation between potential energy and molecular shape. The molecular shape is modelled by means of fused-spheres (the so-called van der Waals surfaces), which are characterized in the context of the shape group method. This model surface is known to mimic reasonably well the shape features of more realistic molecular surfaces, such as electronic isodensity contours [14]. A van der Waals surface is the envelope surface obtained by the superposition of atomic spheres of fixed radii, and, as such, it constitutes a convenient model, since it can be studied analytically. In this model no knowledge of van der Waals forces is required.

The molecular shape is described dynamically by following the change in the surface's topological descriptors along conformational rearrangements. Thus, the conformational subset can be divided into *shape invariance regions*, i.e., domains in configuration space where the shape of the molecular surface remains essentially the same, while minor motions are allowed. It is worth remarking that these domains are defined *in terms of the shape of a molecular surface, and do not require the knowledge of the total energy nor the repulsive forces within the molecule*. Comparison of these shape invariance maps with potential energy maps provides a quantitative relation between energy, shape, and nuclear configurations.

The series of the three structural isomers of dihydroxybenzene are considered as examples, with nonrigid OH torsional paths computed at the STO-3G *ab initio* level. The three isomers provide appropriate examples since their potential energy surfaces exhibit different features, due to the different distances between the two hydroxylic groups.

The article is organized as follows. In Sect. 2 we discuss the model systems considered, as well as the computation of the potential energy surface and the characterization of molecular shape. In Sect. 3 we show the results for the energy maps and shape invariance maps, and the general observations are summarized. Further comments on molecular shape-energy relations are found in Sect. 4.

2. Model systems: two-dimensional conformational problems

In order to study some explicit relationships between potential energy and molecular shape, we have considered a two-dimensional conformational subset of nuclear configurations. To this purpose, molecules exhibiting two internal rotors are taken as illustrative examples.

The molecules considered are 1,2-dihydroxybenzene (catechol), 1,3-dihydroxybenzene (resorcinol), and 1,4-dihydrozybenzene (hydroquinone). The shapes of these systems, undergoing rigid rotations from stationary point geometries, are discussed in detail in [12]. In the present work, we have used partially relaxed geometries, allowing the nonrigidity in the torsion to be taken into account properly.

The subspace of internal coordinates considered is defined as follows. In order to reduce the size of the problem, the angles and bond lengths relating to the carbon and hydrogen atoms of the benzene ring are kept constant at their experimental values for the benzene molecule. The potential energy has been minimized over the remaining subspace of eight internal coordinates for every pair of torsion angles. These coordinates consist of two O–H distances, two C–O distances, two COH bond angles, and two CCO bond angles. This subset of coordinates involves those on which the torsional, nonrigidity effects are the greatest. From the practical point of view, it may be possible that, for some molecules, an even smaller subset could be sufficient to describe the essential features of the relaxed cross section of the potential energy surface. Within this subset the potential energy is minimized at the STO-3G *ab initio* level, using the standard GAUSSIAN 86 program of Pople and coworkers [15]. This approximation level is good enough to obtain reliable geometries and the features of the potential energy surfaces for two-dimensional torsional problems. Regarding the internal degrees of freedom we consider fixed, their variation with substitution has been estimated [16], and it is not expected to alter the conclusions of the present analysis of molecular shape.

The molecular surface associated to each nuclear geometry is modelled by a fused-sphere van der Waals surface (VDWS). These surfaces are currently used to describe the three-dimensional "body" of a molecule. The representation of isoelectronic density contours by means of VDWS's has also been discussed in the literature [14]. The van der Waals envelope surface is the model we employ to characterize the shape of these molecular surfaces, in order to contrast the information provided by shape invariance maps and energy maps. Notice that the construction of a VDWS requires the knowledge of a nuclear geometry within a relaxed cross section, thence, it involves an energy minimization. However, the information provided by these energy minimizations tells one little about the shape features of a molecular surface. We will perform independent studies of molecular shape and energy in configuration space in order to analyze their interrelations.

The procedure employed here to study the shapes of these surfaces, the shape group method (SGM), has been thoroughly discussed earlier [8–12]. For the sake of completeness, a brief discussion is presented here. The characterization of a VDWS is as follows. Let us consider a molecule consisting of N nuclei, with a given configuration $\boldsymbol{K}$ in the reduced nuclear configuration space $\boldsymbol{M}$, $\boldsymbol{K} \in \boldsymbol{M}$ [2]. The torsional rearrangements can be represented as paths within a subset of $\boldsymbol{M}$. The construction of a fused-sphere model requires only a series of atomic radii $(\varrho_1, \varrho_2, \ldots, \varrho_N)$. Let us represent them by a vector $\boldsymbol{\varrho}$:

$$\boldsymbol{\varrho} = (\varrho_1, \varrho_2, \ldots, \varrho_N), \quad \varrho_i > 0. \tag{1}$$

The surface under consideration, indicated as $G(\boldsymbol{K}, \boldsymbol{\varrho})$, is formed by the envelope surface obtained after the superposition of atomic spheres. By changing the nuclear configuration $\boldsymbol{K}$ continuously, we have a continuum of VDWS's. Notice that the change of atomic radii leads to another continuum of molecular surfaces. The role of changing atomic radii, for a fixed nuclear configuration, in modifying the shape of conformationally flexible molecules is discussed in [17]. In our case , we will consider fixed values of van der Waals radii, and focus our attention only on conformational reordering. The values for radii are taken from [18].

In order to provide a concise, algebraic description of $G(\boldsymbol{K}, \boldsymbol{\varrho})$, we derive a series of surfaces $G_n(\boldsymbol{K}, \boldsymbol{\varrho})$ by truncating from $G(\boldsymbol{K}, \boldsymbol{\varrho})$ all spherical n-type faces (n-edged spherical polygons) for some fixed n [10]. If there exists a number ϕ_n of such faces, then we have:

$$G_n(\boldsymbol{K}, \varrho) = G(\boldsymbol{K}, \varrho) \setminus \bigcup_{i=1}^{\phi_n} \boldsymbol{D}_n^{(i)}, \tag{2}$$

where $\boldsymbol{D}_n^{(i)}$ is the ith n-type face. (See [10, 12] for some details about defining these faces). The index n runs from 1 to a maximum number m (corresponding to the largest number of spherical arcs that a spherical face possesses on the surface). In general, the truncated surfaces $G_n(\boldsymbol{K}, \varrho)$ are topologically different from the original surface $G(\boldsymbol{K}, \varrho)$. The proposed characterization of $G(\boldsymbol{K}, \varrho)$ is given by the following two families of discrete descriptors:

$$\boldsymbol{\phi}(G(\boldsymbol{K}, \varrho)) = \{\phi_1, \phi_2, \ldots, \phi_m\}, \tag{3a}$$

$$\boldsymbol{\chi}(G(\boldsymbol{K}, \varrho)) = \{\chi_1, \chi_2, \ldots, \chi_m\}, \tag{3b}$$

where χ_n is the Euler–Poincaré characteristic [19] of the truncated surface $G_n(\boldsymbol{K}, \varrho)$. This topological invariant is a concise descriptor of some of the main features of the surface. However, in some cases it is more informative to use the ranks of homology groups (Betti numbers) of the surfaces $G_n(\boldsymbol{K}, \varrho)$ [8]. Moreover, the shape descriptors (3) do not contain complete information on how the surface is "assembled" from its spherical faces. This information is contained in the incidence matrix between faces [20]. Nevertheless, for our present needs, it will be sufficient to use the Euler–Poincaré characteristic.

If G_n is made of n_d disjoint surfaces, then we will list the Euler–Poincaré characteristic of each piece as follows: $\boldsymbol{\chi}_n = (\chi_{n1}, \chi_{n2}, \ldots, \chi_{nd})$. The informal notation $\boldsymbol{\chi}_n = \varnothing$ is used if G_n is the empty set, that is, if the truncation leaves no surface at all. The computation of the spherical faces on the surface, as well as their classification, can be accomplished algorithmically, using programs developed in our laboratory. We shall focus our attention to the dependences of ϕ and χ on configuration $\boldsymbol{K}$.

Two molecular surfaces, corresponding in general to distinct nuclear configurations $\boldsymbol{K}$ and $\boldsymbol{K}'$, will be regarded as equivalent if and only if they possess the same shape descriptors:

$$G(\boldsymbol{K}, \varrho) \approx G(\boldsymbol{K}', \varrho) \Leftrightarrow \phi(G(\boldsymbol{K}, \varrho)) = \phi(G(\boldsymbol{K}', \varrho)),$$

and

$$\chi(G(\boldsymbol{K}, \varrho)) = \chi(G(\boldsymbol{K}', \varrho)). \tag{4}$$

The configuration space $\boldsymbol{M}$ [2] can therefore be partitioned into subsets including all those configurations having equivalent VDWS's. A shape invariance domain in configuration space, or simply a "shape region" [11, 12], is then given as:

$$\boldsymbol{M}_i(\varrho) = \{\boldsymbol{K} \in \boldsymbol{M} : G(\boldsymbol{K}, \varrho) \approx G(\boldsymbol{K}', \varrho) \approx G_i\}, \quad \boldsymbol{M}_i \subset \boldsymbol{M}, \tag{5}$$

where $\boldsymbol{K}' \in \boldsymbol{M}$ is some reference configuration having the ith shape type.

A domain $\boldsymbol{M}_i$ in configuration space represents a *formal* "chemical species", *defined in terms of molecular shape*. The number and type of shape regions $\boldsymbol{M}_i$ will depend on the molecule considered. The shape-region partitioning of $\boldsymbol{M}$ provides a detailed characterization of the relationships between changes in molecular conformations and molecular shape. In the next section we discuss this partitioning in terms of molecular shape, comparing it with the potential-energy-based definition of chemical species.

3. Comparison of potential energy maps and shape invariance maps

Exploiting the periodicity in the torsional motion, the study of the conformational subset of dihydroxybenzenes can be reduced to the ranges of values $-180^\circ \leqslant \varphi_1, \varphi_2 \leqslant 180^\circ$, for the torsion angles φ_1 and φ_2. The maps obtained have toroidal symmetry, i.e., the points at $\varphi_i = 180^\circ$ can be identified with those corresponding to $\varphi_i = -180^\circ$, for $i = 1,2$. The conformation $(\varphi_1, \varphi_2) = (0, 0)$ corresponds to a planar molecule with the two hydroxylic hydrogen atoms closest to each other, for each of the three isomers studied. For clarity, Fig. 1 shows the molecular skeleton of the 1,2 isomer (catechol) and the convention chosen for the dihedral angles. The same convention is used throughout. Note that in each molecule a unique label is assigned to each atom, and two atoms of the same type (e.g., two hydrogen atoms) are always distinguished. Consequently, symmetrically equivalent configurations such as the pair (0, 180) and (180, 0) are also distinguished. This facilitates comparisons of our examples with derivatives asymmetrically substituted on the ring.

Let us consider first the case of hydroquinone. This represents the simplest of the three systems, since the shape of the molecular surface and the potential energy function exhibit the fewest features. This is due to the fact that the two OH groups are the most distant from each other.

Figure 2 shows the results obtained for the shape invariance region map (Fig. 2a), and the potential energy contour map (Fig. 2b). The letters in the map above represent the various shapes, i.e., families of molecular surfaces with specified shape descriptors (Eqs. (3)). Table 1 summarizes the shape region classification. Both maps have been computed upon scanning the torsion angles by 30° steps. Although the boundaries of the shape regions possess an uncertainty of approximately 15°, they must indeed occur as straight lines. This is so since no superposition of the atomic spheres corresponding to the atoms in the OH takes place at any torsional angle. (See discussion in [12] regarding the boundaries of shape region maps.)

Taking into account the toroidal symmetry, the potential energy map exhibits four different minima, four maxima, and eight saddle points. The pattern in the

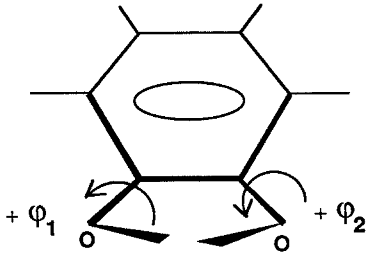

Fig. 1. Skeletal representation of the planar, reference configuration ($\varphi_1 = 0$, $\varphi_2 = 0$) for catechol (1,2-dihydroxybenzene), indicating the sign convention used for torsion angles φ_1 and φ_2. The analogous convention is used for all three structural isomers of dihydroxybenzene

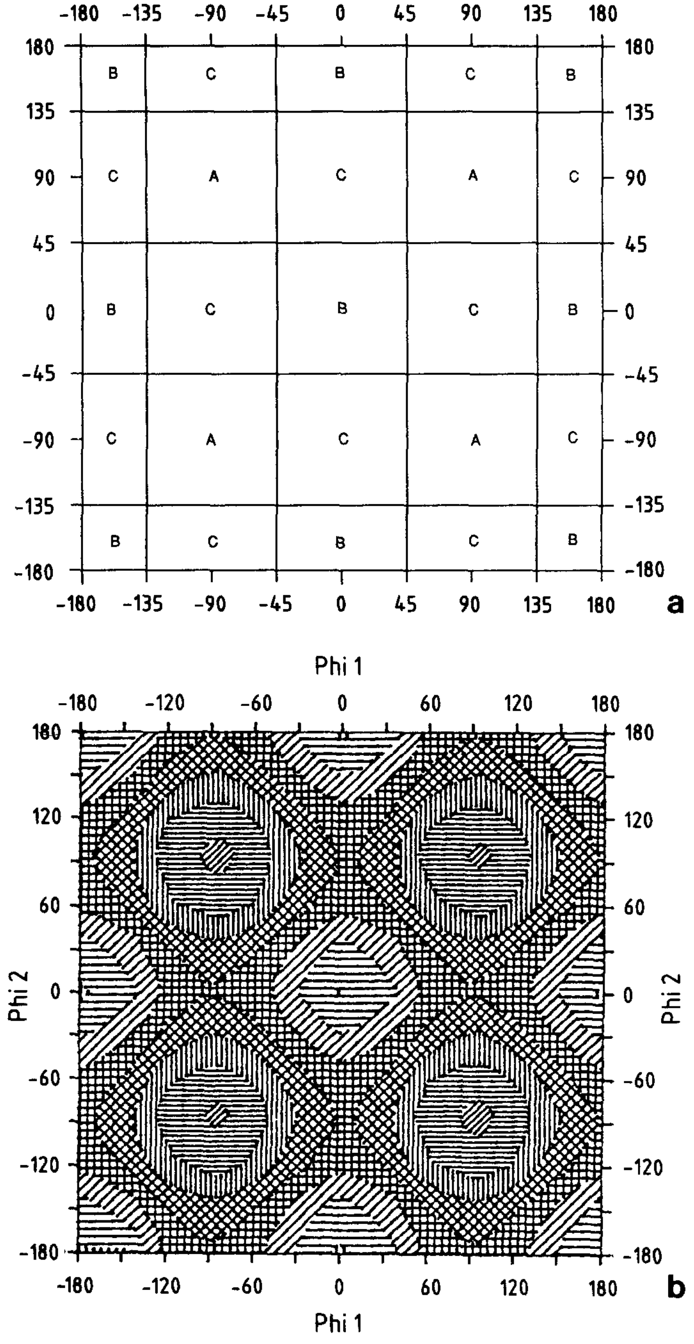

Fig. 2. The potential energy and shape invariance region maps for a hydroquinone molecule (1,4-dihydrozybenzene). Energy given in hartrees, angles given in degrees. Boundaries indicated have an uncertainty of 15°. ▦, Above −375.558; ▨, −375.560 to −375.558; ▤, −375.562 to −375.560; ▥, −375.564 to −375.562; ▩, −375.566 to −375.564; ⊞, −375.568 to −375.568; ▨, −375.570 to −375.568; ▤, −375.572 to −375.570; ▥, below −375.572

Table 1. Shape invariance region classification for the torsional conformational subset of structural isomers of dihydroxybenzene. Shape classification is given only for regions whose shape coincides with that of a critical point

a. Hydroquinone (1,4-dihydroxybenzene)

Shape region	ϕ	χ
A	{4, 10}	{−2, (1, 1, 1, 1)}
B	{4, 0, 0, 12}	{−2, 2, 2, (1, 1, 1, 1)}
C	{4, 5, 0, 6}	{−2, (1, 1), 2, (1, 1, 1)}

b. Resorcinol (1,3-dihydroxybenzene)

Shape region	ϕ	χ
A	{4, 8, 0, 2}	{−2, (1, 1, 1, 1, 1), 2, (1, 1, 1, 1)}
B	{4, 1, 0, 10, 0, 1}	{−2, (1, 1), 2, (1, 1, 1), 2, (1, 1)}
C	{4, 4, 0, 7}	{−2, (1, 1, 0), 2, (1, 1, 1, 1)}
D	{4, 1, 0, 9, 0, 1, 0, 1}	{−2, (1, 1), 2, (1, 1, 1), 2, 1, 2, (1, 1)}
E	{3, 1, 0, 9, 2, 2}	{−1, (1, 1), 2, (1, 1, 1, 0), 0, 0}

c. Catechol (1,2-dihydroxybenzene)

Shape region	ϕ	χ
A	{4, 10}	{−2, (1, 1, 1, 1)}
B	{4, 2, 0, 6, 0, 0, 0, 2}	{−2, (1, 1, 1), 2, (1, 1, 1, −1), 2, 2, 2, 1}
C	{4, 4, 0, 2, 2, 2, 0, 1}	{−2, (1, 1, 1, 0), 2, 1, 0, 0, 2, 1}
D	{4, 2, 0, 10}	{−2, (1, 1, 1), 2, (1, 1, 1)}
E	{4, 4, 2, 4, 0, 2}	{−2, (1, 1, 1, 1, 1), 0, 0, 2, 1}
F	{4, 5, 0, 3, 0, 1, 0, 1}	{−2, (1, 1, 1, 0), 2, (1, 1), 2, 1, 2, 1}

contour map (a planar map) strictly has the symmetry D_{2h}. However, its distortion from a map of symmetry D_{4h} is very minor. Observe, for example, the small difference in the maxima corresponding to the conformations $(\varphi_1, \varphi_2) = (90, -90)$ and $(\varphi_1, \varphi_2) = (90, 90)$; these two conformations correspond to the OH groups perpendicular to the benzene ring, in positions cis and trans, respectively. As the two OH groups are far from each other in hydroquinone, the two conformers have similar energies. Moreover, although the minimum at the $(0, 0)$ conformation is slightly above the others, its catchment region can hardly be distinguished from the ones corresponding to the other minima.

As a comparison, the shape invariance region map possesses strictly D_{4h} symmetry, as a consequence of the fact that the interpenetration pattern of the two, distant OH group fused-sphere models is the same in two planar arrangements $((\varphi_1, \varphi_2) = (0, 0)$ and $(\varphi_1, \varphi_2) = (180, 180))$. In other words, the molecular shape, as defined by the given invariants, is "blind" to the small distortion from the D_{4h} symmetry in the potential energy. Notice that a distinct shape can be associated with every type of critical point: shape "A" (see Table 1a) to the maxima, shape "B" to the minima, and shape "C" to the saddle points. Observe that two, apparently different surfaces, for instance, the two planar minima, are classified as *having the same shape*. This is a fact stemming only from the actual implementation of the SGM: they are classified as having the same shape since they have the same number and type of neighborhood relationships between spherical faces. Other classification schemes, based on different principles, may not have this feature.

This near coincidence between the shape invariance maps and the potential energy contour maps allows us to carry out the analysis from a different point of view. Since the shape of a VDWS mimics very closely the catchment region classification of the potential energy function, the latter can be thought as exhibiting essentially hard-sphere type features. In this sense, the relation between molecular shape (as described by the fused sphere SGM) and potential energy gives one a criterion to establish the importance of the steric repulsive character in the energy contribution.

Figure 3 shows the results for the second isomer, resorcinol. As the two hydroxylic groups become closer, the shape and potential energy maps exhibit new features. The overall pattern of the potential energy map is similar to the one for hydroquinone (the same number of critical points occur), but the deviation from the D_{4h} symmetry is now more pronounced. Notice, for example, the difference between the maxima corresponding to the conformations (90, 90) and (90, -90). Furthermore, the minimum at (0, 0) has become clearly different from the others. These features have similar counterparts in the shape invariance map (Fig. 3a). The symmetry of the map is now D_{2h}, slightly distorted from D_{4h}. The shape classification is provided only for the regions whose shape coincides with that of a critical point. (See Table 1b for the classification.)

In the shape map we notice that all the maxima are still classified as having the same shape (shape "A", Table 1b). Yet, the shapes of boundaries differ. Notice that along some directions, a larger distortion is needed to leave the shape region "A" starting from maximum (90, -90), than that required when starting from (90, 90). This difference is consistent with the fact that the former maximum is slightly higher than the latter.

Moreover, the shape of the minimum at (0, 0) (shape "E") is found to be different from the shape of the other minima (shape "B"). This is also consistent with the differences found between the minima in the potential. It is noteworthy that when moving away from the shape "E" region towards a region with a maximum-like shape, the surface exhibits features present in the other minima (shape "B").

Summarizing the above, in the case of resorcinol, a further distortion from the symmetry D_{4h} in the potential energy contour map is accompanied by a similar distortion in the shape invariance map. It is still possible to associate a characteristic shape to every critical point. Moreover, catchment regions (for minima) of different sizes correspond to molecular surfaces with different shapes. Notice, though, that not every shape invariance region can be associated to a critical point (see regions without a letter in Fig. 3). In other words, the surface exhibits some shape characteristics which do not appear to correlate directly with any of the major features of the potential.

For the 1,2 isomer (catecol) one has the strongest interaction between hydroxylic groups during the internal rotations. Accordingly, this molecule exhibits

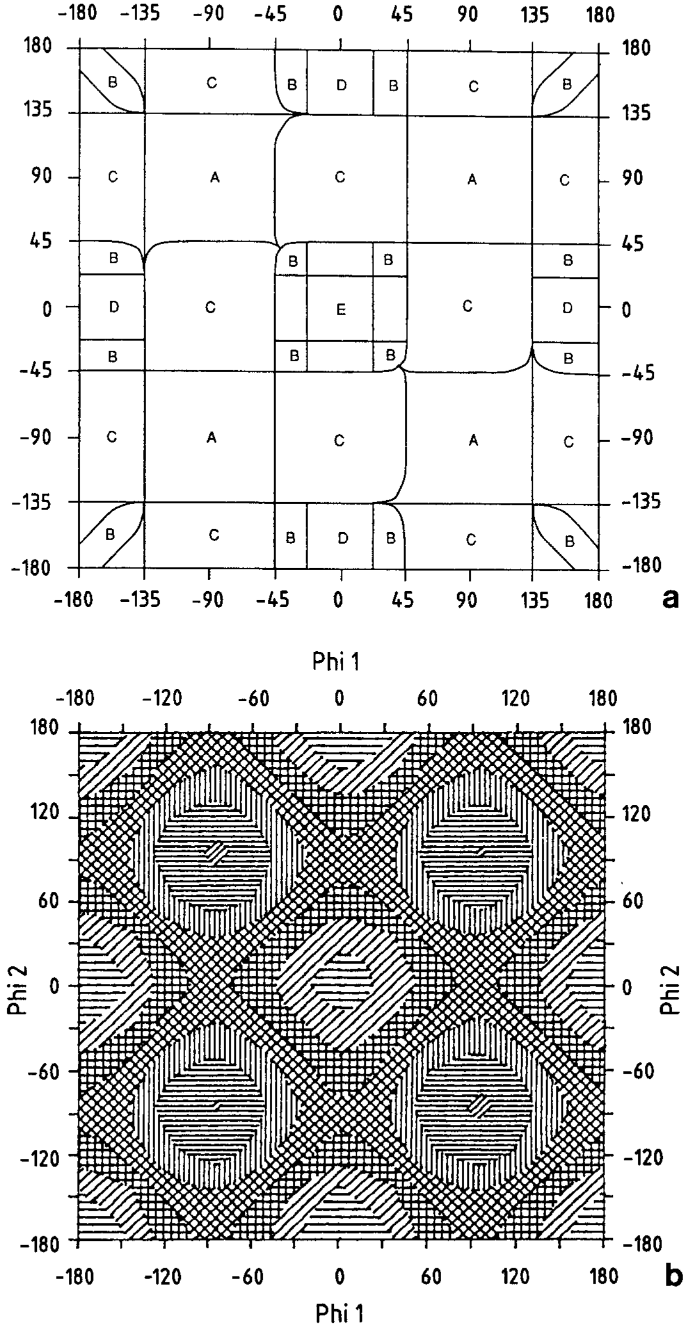

Fig. 3. The potential energy and shape invariance region maps for a resorcinol molecule (1,3-dihydroxybenzene). Energy given in hartrees, angles given in degrees. Boundaries indicated have an uncertainty of 15°. ▦, Above −375.557; ▨, −375.560 to −375.557; ▤, −375.562 to −375.560; ▥, −375.565 to −375.562; ▩, −375.567 to −375.565; ⊞, −375.570 to −375.567; ▨, −375.572 −375.570; ▤, −375.575 to −375.572; ▥, below −375.575

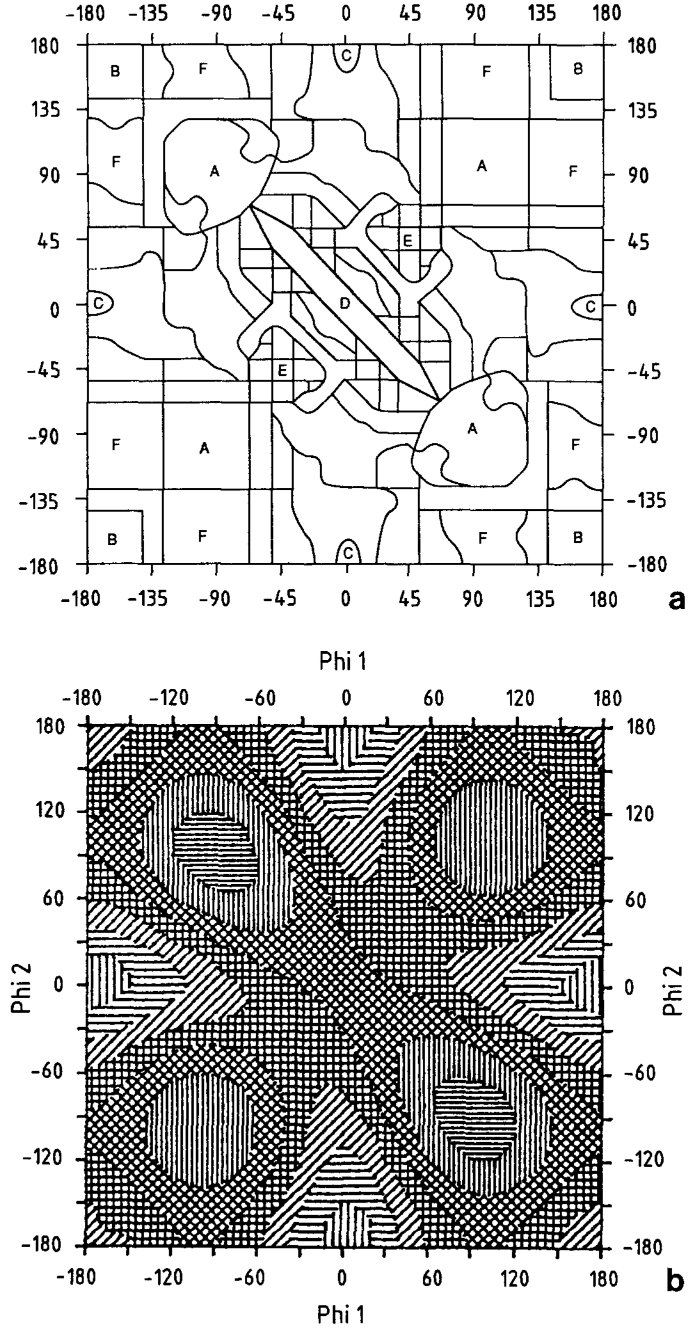

Fig. 4. The potential energy and shape invariance region maps for a catechol molecule (1,2-dihydroxybenzene). Energy given in hartrees, angles given in degrees. Boundaries indicated have an uncertainty of 7°. ▦, Above −375.552; ▨, −375.55 to −375.552; ▤, −375.558 to −375.555; ▥, −375.561 to −375.558; ▩, −375.564 to −375.561; ▦, −375.567 to −375.564; ▨, −375.570 to −375.567; ▤, −375.573 to −375.570; ▥, below −375.573

very different features, both in its molecular shape and potential energy function during torsional motion, when compared with the other two isomers.

Figure 4a shows the results for the shape map and the potential energy contour map. Notice that the number of critical points has changed. Considering the toroidal symmetry in the subset, the energy contour map has three minima instead of four. The shallower minimum in (0, 0) found in resorcinol has now become a saddle point. Also the number of saddle points has been reduced from eight to seven, since two saddle points and a minimum have degenerated, forming a single saddle point. The number of maxima is still four.

The distortion from the D_{4h} symmetry in both shape and energy contour maps is evident. The difference between the maxima (nonplanar conformations) at (90, 90) and (90, −90) is very pronounced. The minima (planar conformations) at (−180, 0) and (0, 180) have catchment regions aligned differently with respect to the coordinate axes. The shape invariance region map shows some features consistent with the potential contour map, as well as some differences. Due to the larger number of features, this map has been computed with greater accuracy. The estimated error in the shape region boundaries should not exceed 7°.

Firstly, one notices that the symmetry in both maps of Fig. 4 is the same. The shape of the minima at (−180, 0) and (0, 180) (shape "C", see Table 1c) is different from that of the minimum at (−180, 180) (shape "B"), and similar comparisons are obtained in the potential energy contour. All maxima are still assigned to have associated molecular surfaces with the same shape (shape "A"), though the boundaries of their shape regions are different.

Regarding the saddle points, all those that are of different energy according to the potential are also classified into different shape regions (shapes "F", "E", and "D"). Notice that the boundary lines for shape regions near the saddle points at (0, 0) and (38, 38) [21] are curved and quite involved. These features are due to the complicated interpenetration of the atomic spheres for the atoms in the OH groups, which are moving away from each other, while the other internal coordinates relax. In agreement with these observations, the upper right corner of the shape region map exhibits more straight line boundaries than those in the upper left corner, which tend to be curved.

Although it is possible to classify the critical points according to the shapes of their corresponding molecular surfaces, there are numerous shape regions not associated with any of the main features of the potential energy function. As suggested by the cases of catechol and resorcinol, the number of shape regions seems to be greater in the neighborhood of saddle points. The shape of fused-sphere molecular surfaces may undergo a larger number of essential changes when the nuclear configuration is close to a saddle point.

4. Further comments and conclusions

The examples analyzed in the previous section provide some clues to the understanding of the relationships between changes in molecular shape and changes in potential energy induced by conformational reorderings.

As observed, the pattern of distribution of shape invariance regions follows closely the potential energy features. That is, different types of critical points are associated with molecular surfaces which have different shapes. Moreover, the extent and shape of the catchment regions for stationary points can be comparable with the extent and shape of an associated shape invariance region. To our knowledge, no previous quantitative analysis had shown that one could associate molecular surfaces of different shape features with different critical points on the potential energy hypersurface.

However, the molecular shape can be "blind" to the occurrence of certain features of the potential. For example, critical points of the same type, but with different geometries, can have associated molecular surfaces of equivalent shapes. On the other hand, molecular surfaces can exhibit shape changes that do not correspond to any of the main features of the potential. These shape changes can be physically meaningful, since they may correspond to major rearrangements of atoms occurring along a conformational change in which the potential energy varies monotonously. Cases like this have been found in some intermediate geometries between maxima and minima for one-dimensional torsional problems [17].

Summarizing the above, chemical processes are dependent not only on the change in energy content, but also on the shape of the spatial arrangement of atomic nuclei within a molecular system. Quantum mechanics provides an accurate method for determining how the energy changes in a molecule, but provides only indirect information about molecular shape, since the classically motivated concept of molecular shape is in fact alien to rigourous quantum mechanics [22]. Nevertheless, in this work we have shown that shape and energy, which are two relevant aspects to understanding molecular properties, can be related, though in a nontrivial manner. That is, though in a broad sense the molecular shape maps and potential energy maps possess similar structures, each one contains essential information that cannot be deduced from the other.

The location of the boundaries of shape regions vary with the choices of atomic radii. If one allows the radii to vary within some physically meaningful ranges, then the boundaries will become boundary layers between regions. These boundary layers would better represent the fuzzy nature of molecular species [2, 23] and molecular surfaces. Some results along this line have been studied in [17] for one-dimensional torsional problems.

The method followed in this work, based on a topological classification of surfaces derived from fused-sphere models, provides a simple quantitative expression for the relations between shape and potential energy. The use of the topological invariants $\phi(G(\boldsymbol{K}, \varrho))$ and $\chi(G(\boldsymbol{K}, \varrho))$ is sufficiently informative to classify molecular shapes in the cases studied.

The present description also leads to shape invariance regions that are not very different from the potential energy catchment regions. The analysis performed in this paper, by using the dihydroxybenzenes as illustrative examples, shows this relationship between catchment regions and shape invariance regions for the first time. This near coincidence suggests that the structure of some conformational surfaces may be approximated in terms of interrelations of atomic spheres. Actually, the quality of such an approximation could be measured in terms of the degree of similarity between the shape maps and the energy contour maps. In this sense, the potential energy function for hydroquinone should be modelled very accurately by considering the interaction between spheres in a van der Waals surface. For the other two isomers, however, the maps of potential energy and shape show important differences.

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