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Molecular electrostatic potential topographical studies on the structural motifs of C_{60} reveal unusual features. Ethylene, [5]radialene and corannulene are predicted to be structural motifs present in C_{60} . However, benzene does not fit into this framework. The double bonds in all the above molecules are activated upon pyramidalization at the carbon centre, the extent depending on the anisotropic environment of the conjugated carbon. The peripheral double bonds in corannulene are predicted to be more susceptible to electrophilic attack in comparison to the exocyclic double bonds of the five-membered ring.

Introduction

The wrapping of graphite by laser induced vaporization produces a new molecular allotrope of carbon, fullerene with a spheroidal geometry.¹ This geometrical aspect of fullerene compels a pyramidalized carbon network on the curved surface, which otherwise is planar in graphite. Consequently, the extensive π -delocalization enjoyed in graphite is inhibited in the non-planar C_{60} .^{2,3} This has a profound influence on the structure and reactivity of C_{60} . The unequal C–C bond lengths in the six-membered rings of C_{60} as calculated theoretically (1.446; 1.401 Å)^{4,5} indicate considerable localization from the structural point of view. Further, the tendency of C_{60} to undergo facile electrophilic addition reactions like the Lewis acid mediated arylation,⁶ osmylation⁷ and halogenation,^{6,8} reveals unequivocally the localized π -character of the double bonds.^{9,10} Theoretical estimates of the diamagnetic susceptibility at the carbon centres in C_{60} at various levels indicated that C_{60} is much less aromatic than benzene.¹¹ Unlike benzene, it was predicted that the exaltation magnetic susceptibility will be higher in C_{60} anions. Arguments from energetics and reactivity also point to the largely localized behaviour of the double bonds.¹² Is localization a consequence of the pyramidalized network in C_{60} ? While the decrease in π -bonding with distortions in the sp^2 centre is known, the present study gives a quantitative picture of the consequences of the pyramidalization at the carbon in C_{60} . *Ab initio* calculations coupled with the molecular electrostatic potential (MESP) topographical studies on the distorted structural motifs—ethylene (1a,b), benzene (2a,b), [5]radialene (3a,b) and corannulene (4a,b) present in C_{60} provide an insight into the origin of such effects and their interrelation with C_{60} .

Method of calculation

The geometries of the fragments were optimized at the HF/6-31G* level of theory using GAUSSIAN92 program package,¹³ within the given symmetry restriction, for fixed values of the pyramidalization angle, θ (90° – 120° ; Fig 1). Single point calculations employing 6-31G** basis, at HF level, on the HF/6-31G* optimized geometries were performed using the INDMOL package.¹⁴ The MESP topographical analyses were carried out using the program INDPROP.¹⁵

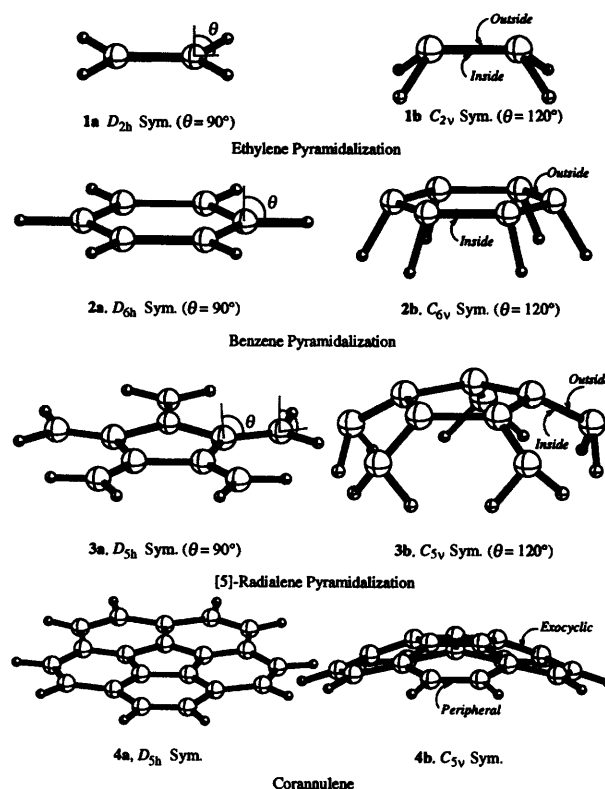


Fig. 1 Structures of planar and distorted ethylene (1a,b), benzene (2a,b), [5]radialene (3a,b) and corannulene (4a,b). The dotted lines in the structures represent the pyramidalizing angle, θ .

Results and discussion

The MESP based studies have been widely used for investigating electron localization in molecules.^{16,17} Lone pairs and C–C π -bonds are generally reflected as negative valued (3,+3) critical points (CPs).^{16–18} This feature in the MESP topography has never been used, until the present work, for analysing the extent of electron localization upon pyramidalization of ethylene, benzene, [5]radialene and corannulene.

The energetics of the C_{2v} distortion of ethylene are well documented in literature.^{2a,19} However, the MESP topography

reveals several features in the process of pyramidalization of ethylene. Two (3,+3) CPs lying on either side of the molecular plane were located for planar ethylene (**1a**: D_{2h}) with an MESP value of -0.0382 au (Table 1). Pyramidalization along the C_{2v} axis leads to two unsymmetrical environments with respect to the plane containing the C–C bond (labelled inside and outside, Fig. 1). As a result, the electron density is unevenly distributed on either side. The variation in the magnitudes of the MESP values at the (3,+3) CPs as a function of θ is given in Table 1. The MESP value for the inside minimum increases continuously and changes character with increasing pyramidalization. This suggests that there is no electron localization on the inside at larger θ . On the other hand, the outside minimum exhibits marginal decrease in the MESP value initially which rises gradually upon increasing pyramidalization. This topographical feature can be understood from the orbital diagram in Scheme 1.

The π -orbitals in planar ethylene are symmetrically disposed on either side of the molecular plane (Scheme 1: **A**). Pyramidalization leads to rehybridized π -orbitals that are splayed largely on the outside leading to better π -overlap (Scheme 1: **B**). This is reflected in the decrease of the MESP value initially, in comparison to planar ethylene (Table 1). Increasing pyramidalization directs the orbital lobes away from each other (Scheme 1: **C**) leading to an increase in the MESP value at the (3,+3) CP outside (Table 1) for larger angles of θ . The decrease in the MESP value in pyramidalized ethylene for smaller θ suggests that the π -bonds are activated, and hence more susceptible towards electrophilic attack, than the planar form. It is also noteworthy that the MESP value calculated on the outside for pyramidalized ethylene at the same angle of the pyramidalized double bonds in C_{60} (11.6° out of the plane of C=C; $\theta = 101.6^\circ$)^{2a} is deeper than that of planar ethylene. However, earlier studies on C_{60} predicted an MESP value of -0.0042 au for the double bonds.³ This discrepancy in the MESP for C_{60} and pyramidalized ethylene is due to the presence of a C–H bond in ethylene in the place of a C–C bond (as in C_{60}). As a

result, the environment at the carbon centre is anisotropic and thereby places a limitation on ethylene as a model.

In contrast to ethylene, pyramidalization of benzene (**2a**, **2b**) along the C_6 axis shows different topographical features. Six (3,+3) CPs for the six C–C bonds were located on either side of the C_6 ring plane (Fig. 1). The MESP values for benzene, however, are larger (-0.0324 au) in comparison to that of ethylene (-0.0382 au), a consequence of π -delocalization. Pyramidalization reveals a steady increase in the MESP value for the outside and inside CPs (Table 1). The MESP values for various angles of θ indicate the outside minimum to be deeper than the inside. Further, all six CPs corresponding to the outside minimum are retained upon pyramidalization. This suggests that the π -delocalization is not inhibited by the out-of-plane bending of the ring hydrogens, on the outside. In contrast, the six CPs corresponding to the inside minimum converge to a single one along the C_6 axis for θ starting from 106° .

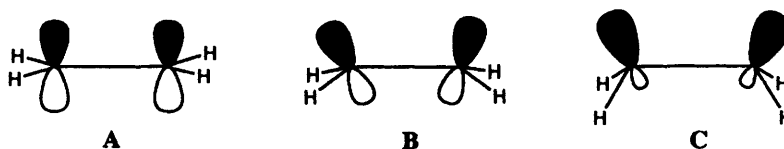
Topographical features similar to that of pyramidalized benzene are anticipated for the curved surface of the six-membered ring in C_{60} . However, an earlier topographical study on C_{60} using different basis sets located only three CPs on the outside of the curved surface of the six-membered ring, in analogy to three localized π -bonds.³ The pattern of the (3,+3) CPs further suggested that the double bonds of the six-membered rings in C_{60} emanate as the exocyclic bonds of the five-membered rings. This is substantiated from a model calculation by pyramidalizing the *exo*-double bonds of [5]radialene.

[5]Radialene (**3a**: D_{5h} symmetry) exhibits five MESP minima (-0.0334 au) for the exocyclic double bonds on either side of the molecular plane. No (3,+3) CP could be located for the C–C bonds corresponding to the five-membered ring. Pyramidalization of these double bonds along the C_5 axis leads to a structure with C_{5v} symmetry (**3b**, Fig. 1). With an unsymmetrical environment around the double bond, the magnitudes of the MESP values at the (3,+3) CP on the outside and inside vary differently as a function of θ (Table 1). The outside minimum becomes deeper than the inside ones upon pyramidalization and

Table 1 MESP values ($\times 10^{-2}$ au) at the (3,+3) CPs for ethylene, benzene and [5]radialene at various pyramidalizing angles θ (degrees)

θ	MESP values for outside CP			MESP values for inside CP		
	Ethylene	Benzene	[5]Radialene	Ethylene	Benzene	[5]Radialene
90	-3.8242	-3.2366	-3.3363	-3.8242	-3.2366	-3.3363
92	-3.9568	-3.2344	-3.4601	-3.6487	-3.2328	-3.1656
94	-4.0480	-3.2278	-3.5454	-3.4289	-3.2240	-2.9550
96	-4.0997	-3.2158	-3.5940	-3.1631	-3.2084	-2.7002
98	-4.1148	-3.1987	-3.5991	-2.8490	-3.1855	-2.3907
100	-4.0933	-3.1778	-3.5719	-2.4893	-3.1561	-2.0331
102	-4.0417	-3.1530	-3.5161	-2.0807	-3.1191	-1.6261
104	-3.9594	-3.1246	-3.4368	-1.6184	-3.0744	-1.1652
106	-3.8531	-3.0920	-3.3420	-1.1060	-3.0170	-0.6537
108	-3.7191	-3.0576	-3.2195	-0.5392	-2.9584	-0.0659
110	-3.5619	-3.0208	-3.1002	0.0742	-2.8881	0.5707
112	-3.3844	-2.9819	-2.9783	0.7282	-2.8057	1.2735
114	-3.1871	-2.9414	-2.8429	1.3846	-2.7106	2.0596
116	-2.9725	-2.8994	-2.7167	<i>a</i>	-2.6023	<i>a</i>
118	-2.7418	-2.8565	-2.6126	<i>a</i>	-2.4801	<i>a</i>
120	-2.4982	-2.8129	-2.5307	<i>a</i>	-2.3432	<i>a</i>

a (3,+3) CP could not be located.



Scheme 1 Schematic representation of the rehybridization of the π -orbitals in ethylene upon pyramidalization

Table 2 MESP values ($\times 10^{-2}$ au) at the (3,+3) CP for corannulene

Symmetry	MESP values for outside CP		MESP values for inside CP	
	Exocyclic	Peripheral	Exocyclic	Peripheral
D_{5h}	-2.5241	-2.9469	-2.5241	-2.9469
C_{5v}	-2.5477	-2.8080	-2.4879	-2.9439

more localized compared to the planar form initially, a feature similar to that of non-planar ethylene. Further, it is interesting to note that the topographical features exhibited by C_{60} around the five-membered rings³ is similar to that of [5]radialene in the non-planar form (3b, Fig. 1). Thus, [5]radialene can be considered as a key structural motif of C_{60} .

The next logical sequence towards C_{60} along the C_5 or radialene route is the addition of a cyclic C_{10} unit leading to corannulene.²⁰ Theoretical²¹ and X-ray diffraction studies²² reveal a bowl-shaped structure (4b) for this hydrocarbon, which exhibits high fluxional behaviour. The bowl-to-bowl inversion of corannulene along the planar D_{5h} symmetric transition state (4a) was calculated to be 8.8 kcal mol⁻¹ (1 cal = 4.184 J) at the HF/6-31G* level of theory.²³ The MESP topography for the planar structure reveals five CPs (on either side of the molecular plane) corresponding to the double bonds exocyclic to the central five-membered ring and five more for the five peripheral double bonds of the six-membered rings (Table 2). The MESP value for the double bonds on the periphery of the molecule (-0.0295 au) is calculated to be deeper compared to bonds exocyclic to the five-membered ring (-0.0252 au; Table 2). Further, only three MESP minima (two from the exocyclic double bond and one from the peripheral bond) corresponding to the three double bonds of the six-membered ring in corannulene could be located. No minima corresponding to the remaining three C-C bonds of the six-membered ring could be traced. This is in striking contrast to that of benzene (where six minima are located for the six C-C bonds), but in agreement with the MESP features exhibited by C_{60} .³ This suggests that the deactivation of π -delocalization in corannulene could be a geometrical consequence of the annelation of the five-membered ring to the six-membered ring, and not due to pyramidalization of the carbon centres. It seems that the tendency of the latter is to activate the π -bond. This is quantified from the topographical features exhibited by corannulene in the bowl-shaped geometry (4b), a structure possessing a curved surface similar to that of C_{60} . In the C_{5v} geometry, the outside minimum is calculated to be deeper (Table 2) than the inside ones for the exocyclic double bonds. In addition, the pyramidalized exocyclic double bonds are activated in comparison to that in the D_{5h} symmetric structure. The peripheral double bonds in 4b with smaller MESP values in corannulene indicate the double bonds to be less reactive than in ethylene and [5]radialene (Tables 1, 2). In general, corannulene retains the characteristics of [5]radialene in the pyramidalized geometry and possesses topographical features similar to those of C_{60} .

Conclusions

In conclusion, MESP topographical studies on the structural motifs of C_{60} , shed light on the extent of delocalization/localization in C_{60} . Various key fragments of C_{60} reveal the following aspects.

(i) Ethylene, [5]radialene and corannulene are predicted to be the structural motifs present in C_{60} . However, benzene may not serve as a typical motif for this purpose.

(ii) In general, double bonds are activated upon pyramidalization.

(iii) Deactivation of the π -bonds in the six-membered ring in corannulene is attributed to the geometrical consequence of the annelation of the five-membered ring to the six-membered ring.

(iv) The peripheral double bonds in corannulene (4b) are predicted to be more susceptible towards electrophilic attack compared to the exocyclic double bonds. Thus, appropriate functionalization of the peripheral bonds would help towards a tailor-made synthetic approach to C_{60} .

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