Aromaticity Interplay between Quinodimethanes and C_{60} in Diels−Alder Reactions: Insights from a Theoretical Study

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A theoretical study is performed of the Diels−Alder reactions of various *o*-quinodimethanes (QDM) with C_{60} by the AM1 model and limited ab initio and DFT techniques. All reactions are shown to proceed through a concerted transition state possessing a considerable net aromaticity as evidenced from bond orders and magnetic criteria such as the magnetic susceptibility exhaltations (MSE) and nucleus independent chemical shifts (NICS) and produce different kinds of aromatic stabilized fullerene cycloadducts. Computations show that a strong LUMO-dienophile control of C_{60} is realized by the influence of pyramidalization, but its high reactivity over alkene appears to be governed by the global aromaticity on fullerene rather than its strain. The aromatic functionalization occurring in QDM upon cycloaddition drastically increases the reaction rate and exothermicity of all QDM-C_{60} reactions as compared to the butadiene-C_{60} reaction. In fact, the simultaneously existing aromatic destabilization in fullerene indicates its opposite effect to the resonance stabilization in diene; it is thus fully restricted when the gained aromaticity is transmitted from the nucleophilic QDM to the fullerene electrophile in a push−pull manner. However, the overall aromaticity effect shown by the aromatization as well as the aromaticity of C_{60} seems to accelerate these reactions at an increased rate.

1. Introduction

Recent interest in fullerene chemistry has extensively been focused on the functionalization of C_{60}[1] since the availability of macroscopic quantities of fullerenes.[2] It is now clear that the electron-deficient character[3] of C_{60} stems from its low-lying LUMO; all embedded olefins (6−6 ring junctions) in the fullerene cage thus behave as strong electrophiles. This prompted the development of numerous efficient Diels−Alder cycloadditions[4] rather than other fullerene derivatization processes. The Diels−Alder functionalization of C_{60} has recently been studied kinetically,[5] but few theoretical reports[6] on the mechanism of these reactions provide a definitive explanation for the reactivity of fullerenes. On the other hand, the elusive intermediates, quinodimethanes (QDMs),[7] have been proven to be synthetically fascinating dienes in Diels−Alder reactions, which prompted their use in various natural product syntheses.[7a,8] Their tremendous performance in these reactions is due to the annelation of aromatic systems during the adduct formation, strength-

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ening the progress of the reaction by aromatization. As a result, QDMs have undergone Diels−Alder reactions with C_{60} very easily, leading to a wide variety of aromatic systems involving fullerene-based cycloadducts.[7l,9]

Both QDM and C_{60} have demonstrated from excellent activities in Diels−Alder processes,[7l,9] but the different factors influencing the reaction mechanism still remain unclear. Although QDM reactions were the subject of several theoretical studies,[10] the high reactivity of these dienes through a high degree of aromatization of both TS and reaction product was only recently explored in detail by our computations.[11] Moreover, a process of dearomatization occurring at the reacting bond abutted by two aromatic rings in C_{60} as well as a global aromaticity effect in the fullerene appear to facilitate the reaction. This has not been pointed out in previous reports.[6] Consequently, the combination of both unique processes—aromatic stabilization and destablization—happening in the reaction between QDM and a fullerene thus highlights a push−pull aromaticity effect upon interaction of the electron-donating diene and electron-accepting dienophile. The present work is therefore aimed at studying the reactions of different QDMs, **A**−**F**, with C_{60}, including the butadiene(BD)−C_{60} reaction, to predict theoretically the overall aromaticity influence on the reaction barrier by analyzing the individual effects quoted above. When studying the reactivity−aromaticity relationship of the fullerene, a comparison is made with the prototypical cycloadditions involving ethylene. The main point of interest in this study is to address the "aromaticity resistance" in QDM−fullerene reactions and how it is overwhelmed by the global aromaticity of the fullerene system and, through this, analyze the relative Diels−Alder efficiency.

2. Method of Computations

Calculations were performed for the Diels−Alder addition of various QDMs to C_{60} by using the semiempirical AM1 Hamiltonian[12] implemented in the MOPAC 6.0 program.[13] The stationary point structures were fully optimized using Baker's eigenvector following (EF) procedure.[14] The large size of fullerene cages involved in the reactions restricted the use of currently familiar ab initio and density functional theory (DFT) techniques. However, optimizations at the B3LYP/6-31G* level[15] and single point computations at B3LYP/3-21G[15] on AM1 geometry were done for the ethylene and C_{60} reactions, respectively, using Gaussian 94[16] to show the reliability of the AM1 model. The single imaginary frequency of TS has been checked by vibrational analysis. To quantify the aromaticity factor, the magnetic susceptibility exaltation (MSE)[17] as well as nucleus independent chemical shift (NICS)[18] criteria were used. Accordingly, the NMR-related properties involving magnetic susceptibilities and diamagnetic shieldings were calculated, respectively, using CSGT and GIAO methods[19] at the HF/3-21G level[15a] with AM1 geometry. The MSEs of TS (Λ_{TS}) and product (Λ_P) were obtained by using both reactants as reference systems.[20]

To follow the progress of the reaction, the extent of bond formation and cleavage of each bond, viz., i or j (BF_i and BC_j) at the TS has been calculated from the bond orders[21] as given below. The average percentage of bond formation (BF_{av}), bond cleavage (BC_{av}), and bond make-break (BFC_{av}) at the TS has also been obtained.

$$BF_i \text{ or } BC_j = \frac{BO_{i/j}{}^{TS} - BO_{i/j}{}^{R}}{BO_{i/j}{}^{P} - BO_{i/j}{}^{R}} \times 100 \tag{1}$$

$$BF_{av} = 1/n_i \sum BF_i; \quad BC_{av} = 1/n_j \sum BC_j \tag{2}$$

$$BFC_{av} = \frac{(BF_{av} + BC_{av})}{2} \tag{3}$$

The "earliness" and "lateness" of the TS can be deduced from these indices as described in the earlier reports.[6f,10c,22]

3. Results and Discussion

The earlier treatments of AM1[6,10,22b,c,24] on the mechanism of several Diels−Alder cycloadditions are often shown to yield reliable TSs when compared with high level calculations.[23] The corresponding barriers were seen to be reliable too; especially, the activation energy of the prototype BD−ethylene reaction is found to be 23.2 kcal mol^{-1}, in good agreement with the experimental (27.5 kcal mol^{-1}) and ab initio[23a,b] and DFT values[23c,d] (18−29

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Table 1. Activation and Reaction Energies (kcal mol^{-1}) Calculated at AM1 and B3LYP/6-31G * Levels for Diels−Alder Reactions of Various Quinodimethanes (A−F) with Ethylene; MSEs (ppm, cgs) of Product and TS Calculated at HF/3-21G//AM1 Level Are Also Given

	$\Delta E^{\ddagger}$		ΔE_r			
reaction	AM1	B3LYP/ 6-31G*	AM1	B3LYP/ 6-31G*	Λ_{TS}	Λ_P
BD + ethylene	23.2	22.4	−58.0	−43.1	−18.5	−5.1
A + ethylene	14.8	8.5	−77.0	−70.9	−27.6	−20.6
B + ethylene	24.5	11.5	−55.7	−50.3	−18.9	−17.2
C + ethylene	14.5	7.7	−76.2	−71.9	−26.5	−17.7
D + ethylene	13.	7.6	−77.5	−72.3	−28.0	−19.6
E + ethylene	22.5	15.6	−60.0	−54.7	−22.1	−12.3
F + ethylene	19.1	13.7	−65.5	−57.7	−23.3	−14.5

kcal mol^{-1} at correlated levels). In addition, the trend in reaction energetics calculated for a series of QDM−ethylene reactions at the AM1 level is reproduced by the B3LYP/6-31G* energies (Table 1); it is however known that the AM1 method usually overestimates exothermicities,[23] as is also clear from the values in Table 1.

The whole of these results incited us to use the AM1 method to deal with the current Diels−Alder reactions. However, it has to be remarked that the AM1 barrier for the reaction of compound B in Table 1 is far from the B3LYP/6-31G* value, probably as a result of an underperformance of the AM1 method due to the oxygen present in the reacting function.

Transition Structure. The Diels−Alder reactions of various QDMs (**A**−**F**) with C_{60} shown in Figure 1 produce a variety of aromatic ring-fused fullerene cycloadducts via a concerted mechanism. The reactions involving **A** and **D** follow a synchronous pathway through $\mathbf{TS_A}$ and $\mathbf{TS_D}$ (Figure 2) respectively, while the remaining QDM reactions attain asynchronous TSs ($\mathbf{TS_B}$, $\mathbf{TS_C}$, $\mathbf{TS_E}$, and $\mathbf{TS_F}$). The symmetric and asymmetric approach of QDMs, either by the ring or the diene unit, to a fullerene in the reaction broadly differentiates the corresponding synchronous or asynchronous nature of the TSs, respectively, as can be seen from the bond parameters. It appears that the aromatic stabilization existing in the QDM−C_{60} reactions tends to increase the rate of bond forming and cleaving process at the TS if one compares the TS of simple BD−C_{60} reaction ($\mathbf{TS_t}$). Consequently, the forming bonds (2−3, 4−5, and 1−6) are found to be much weaker, whereas the cleaving bonds (1−2, 3−4, and 5−6) are slightly stronger in the TSs of QDM−fullerene reactions in relation to $\mathbf{TS_t}$. This generalizes the fact that the weakness of forming bonds and the tightness of cleaving bonds assign a high degree of bond make-break at the TS as predicted on the basis of bond distances (Figure 2). The bond criteria thus reveal that the title reactions secure the "early" matured TSs compared to the TS of the BD−fullerene reaction. This is further supported by the percentages of bond formation and cleavage at the TS as shown in Table 2. The early maturation of formed and cleaved bonds of $\mathbf{TS_A}$−$\mathbf{TS_F}$ over $\mathbf{TS_t}$ can be evaluated from the bond order indices (BF_i and BC_j) through their smaller values found in the former TSs and the largest values in a latter case. Furthermore, the "early"/"late" nature of the TSs of the reactions involving **A** and **B** can be justified from the relative aromatization in the QDM ring upon TS formation. The aromatized cyclic functions in the reactions are the derivatives of benzene, pyrimidine, pyrazine, furan, and thiophene. On the basis of the aromaticity trend found in these simple compounds[25] one can expect an increasing order of "earliness" of the TS: $\mathbf{TS_A} > \mathbf{TS_D} > \mathbf{TS_C} > \mathbf{TS_F} > \mathbf{TS_E}$. Both bond parameters (Figure 2) and bond order analysis (Table 2), nicely bookkeep such an "early" type of TS involving the relatively fast matured bonds bearing less percentage of bond make-break. This further indicates the fact that a high aromaticity achieved by the proximal ring of QDM in the reaction greatly increases the extent of bond formation and cleavage at the TS. The TS formation due to **B**−C_{60} reaction leads to a very "late" TS ($\mathbf{TS_B}$) relative to others as predicted by the highest value of BFC_{av}. This may be due to the oxy-functional group of QDM (**B**), which appears to reduce the aromaticity of the benzene ring by lone-pair repulsion during the reaction.

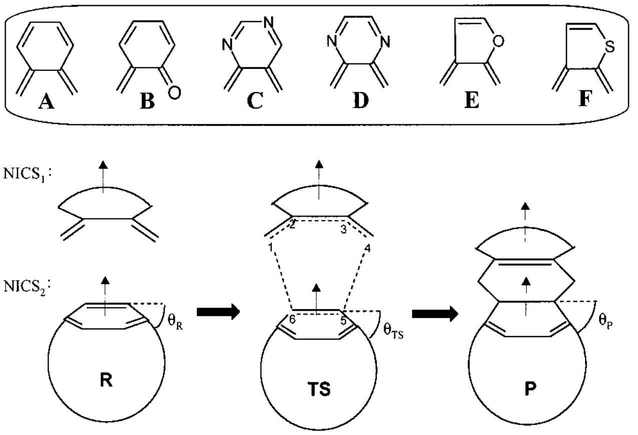

Figure 1. Schematic representation of the aromatization occurring in quinodimethane and dearomatization in the fullerene upon reaction as monitored by the NICS indices calculated 1 Å above the ring. The strain release in fullerene is simultaneously noticed from the changes in the pyramidalization occurring at the reacting centers (angle with respect to the plane of five-membered ring).

Although the reaction between **B** and the fullerene attains some aromatic character in the TS and the final product, it shows a reduced aromaticity upon comparison with **A**, probably due to the presence of the oxygen atom lone pair in the reacting function, leading to a higher reaction barrier and decreased exothermicity. The huge difference between the activation barriers of the two reactions could, however, also be due to an underperformance of the AM1 method for this compound, as also witnessed in the reaction of this compound with ethylene.

In addition, the earliness of the transition states was probed using the pyramidalization angles obtained from using the π-orbital axis vector (POAV) analysis.[26] The mean pyramidalization angles for the transition states (i.e., the average of the pyrimidalization angles of the two

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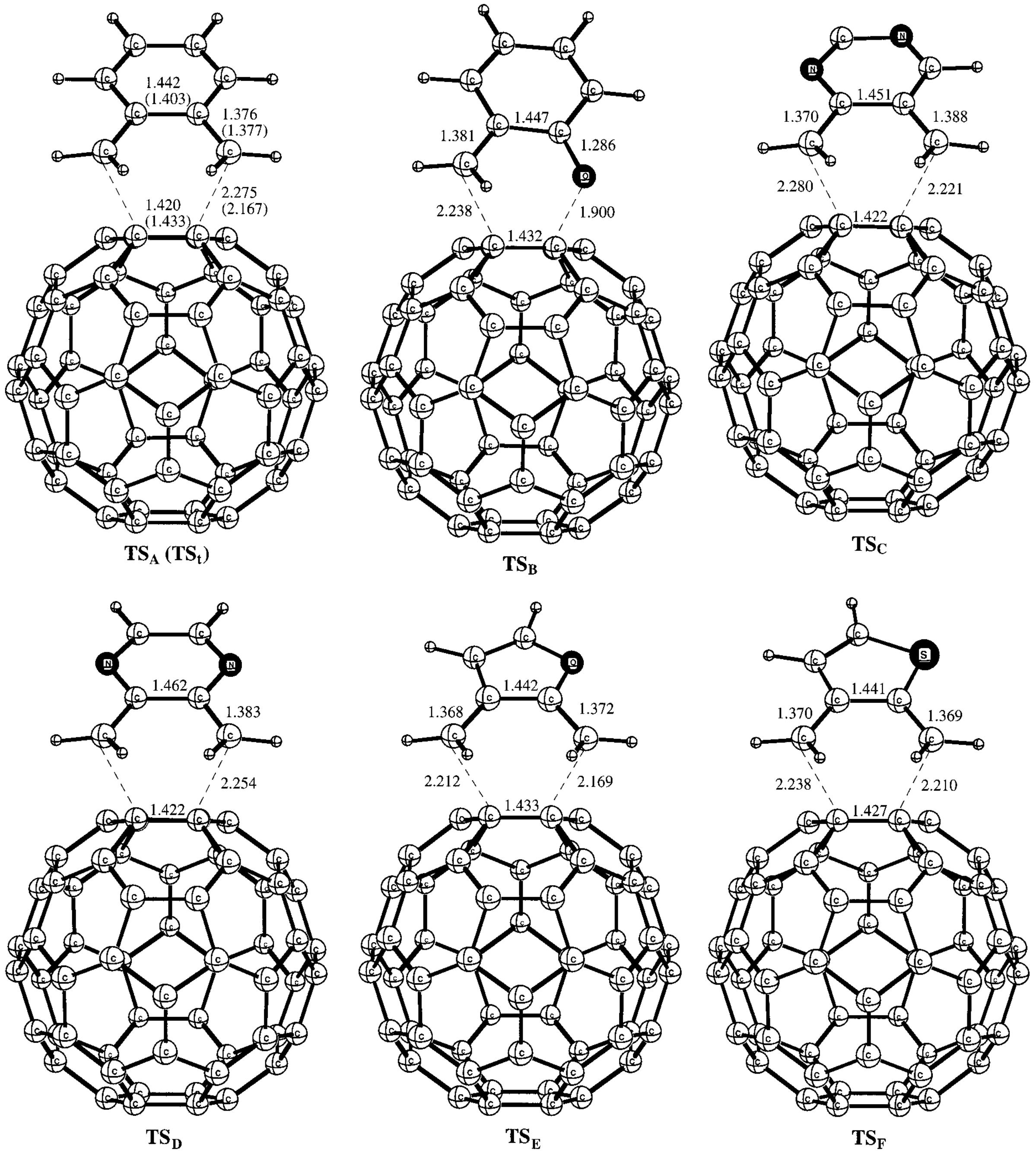

Figure 2. AM1 optimized TSs of the reaction between quinodimethanes (**A**−**F**) and C_{60} and the distances of formed and cleaved bonds; $\mathbf{TS_t}$ refers to the BD−C_{60} reaction.

Table 2. Percentages of Bond Formation and Cleavage at the TS, Their Average Values, and the Average Pyramidalization Angle θ_{POAV} from the π-Orbital Axis Vector Analysis

TS	BC_{1-2}	BF_{2-3}	BC_{3-4}	BF_{4-5}	BC_{5-6}	BF_{6-1}	BF_{av}	BC_{av}	BFC_{av}	θ_{POAV}
$\mathbf{TS_t}$	47.1	37.6	47.1	38.3	47.6	38.3	38.1	47.3	42.7	
$\mathbf{TS_A}$	34.0	36.1	34.0	23.6	30.3	23.6	27.8	32.8	30.3	13.85
$\mathbf{TS_B}$	42.5	44.0	40.2	25.6	39.6	34.4	34.7	40.8	37.7	14.30
$\mathbf{TS_C}$	34.1	39.6	38.4	27.6	31.8	23.5	30.2	37.8	34.0	13.94
$\mathbf{TS_D}$	35.4	40.4	35.4	24.8	30.6	24.8	30.0	33.8	31.9	13.90
$\mathbf{TS_E}$	41.3	30.9	44.1	33.4	39.8	30.2	31.5	41.7	36.6	14.48
$\mathbf{TS_F}$	38.0	29.7	39.7	29.5	36.6	27.3	28.8	38.1	34.5	14.19

carbons of the fullerene on which the diene is added) can be found in Table 2. As can be seen, the lowest pyramidalization angle is found for the TS of compound A, indicating that it possesses the earliest TS. Moreover, one can immediately see that the sequence generated by these values is the same as the one predicted on the basis of bond order analysis.

Does Aromaticity of C_{60} Control the Reaction? The electron-deficient nature of an isolated fullerene is subsequently described on the basis of pyramidalization[3a,27] in the strained π-carbon network. Calculations reveal that the double bonds of C_{60} acquire their remarkable electrophilic behavior through the relatively low-lying LUMO of the fullerene (−2.95 eV) as compared to

Table 3. Calculated FMO Gaps (eV) at the AM1 Level, and Relative Energies (kcal mol^{-1}) Obtained from AM1[B3LYP/3-21G//AM1] for the Reactions of Quinodimethanes A−F with C_{60}; MSEs of TS and Product (ppm, cgs) Calculated at HF/3-21G//AM1 Are Also Given

reaction	$\Delta E_1{}^a$	$\Delta E_2{}^b$	$\Delta E^\ddagger$	Λ_{TS}	ΔE_r	Λ_P
BD + C_{60}	6.4	10.1	16.3 [11.5]	−23.3	−50.8 [−28.3]	−21.0
A + C_{60}	5.3	9.1	9.8 [−1.2]	−32.9	−71.4 [−71.2]	−33.8
B + C_{60}	6.3	8.6	22.4 [3.8]	−26.6	−41.9 [−34.3]	−33.1
C + C_{60}	6.1	8.6	10.7 [1.5]	−29.7	−68.7 [−5.8]	−31.8
D + C_{60}	5.7	8.7	10.2 [0.5]	−33.9	−70.6 [−57.3]	−35.7
E + C_{60}	5.1	9.5	16.0 [6.4]	−27.1	−49.2 [−33.6]	−25.6
F + C_{60}	6.4	9.4	13.0 [6.2]	−30.2	−58.1[−34.4]	−30.1

[a] $\Delta E_{\mathrm{HOMO}}{}^{\mathrm{diene}} - \Delta E_{\mathrm{LUMO}}{}^{\mathrm{fullerene}}$. [b] $\Delta E_{\mathrm{LUMO}}{}^{\mathrm{diene}} - \Delta E_{\mathrm{HOMO}}{}^{\mathrm{fullerene}}$.

Table 4. NICS (ppm) Values along the Reaction Calculated at HF/3-21G//AM1 Level and Pyramidalized Angles (deg) As Indicated in Figure 2

	$NICS_1$			$NICS_2$					
reaction	R	TS	P	R	TS	P	$\theta_R{}^a$	$\theta_{TS}{}^a$	$\theta_P{}^a$
A + C_{60}	−1.7	−7.2	−11.9	−2.0	−1.7	3.1	31.8	37.3	51.0
B + C_{60}	−2.1	−8.0	−11.8	−2.0	−0.5	3.4	31.8	38.4	50.9
C + C_{60}	−2.1	−9.1	−10.9	−2.0	−1.7	3.1	31.8	37.9	51.1
D + C_{60}	−1.9	−7.1	−11.0	−2.0	−1.6	3.1	31.8	37.7	50.9
E + C_{60}	−5.8	−8.3	−10.4	−2.0	−1.7	3.0	31.8	38.9	51.7
F + C_{60}	−5.2	−8.6	−11.6	−2.0	−1.8	3.1	31.8	38.2	51.2

[a] The average pyramidalization angle at the reacting centers of C_{60} and its deviation during the TS and product formation.

ethylene (1.44 eV). Thereby, the π-HOMO of BD and QDMs interacts much more easily with the π*-LUMO of C_{60}, leading to a set of excellent normal electron demand Diels−Alder reactions and this is highly marked by the FMO gaps presented in Table 4. Consequently, the fullerene reactions under investigation exhibit very low barriers (Table 3) as compared to ethylene reactions (Table 1). A high reactivity of C_{60} in a Diels−Alder process can be expected from this observation, and this is most often explained by the effect of pyramidalization of sp^2 carbons.[6] Recently, its high activity is emphasized from the average pyramidalization angles (P_{av}) of all carbons when growing C_{60} from naphthalene via seven bucky-bowls.[6e] A lowering of reactivity from naphthalene to C_{60} in a series of Diels−Alder reaction is found and related to the reduced LUMO energy and the increased P_{av} values. In the same reaction sequence, one can also notice a stepwise increase of net strain as well as aromaticity due to the increasing pyramidalization and number of hexagonal rings respectively in the fullerene. At this point, the electrophilically more reactive C_{60} is explained on the basis of the existence of strain[3] as well as the effect of aromaticity.[3a,28] Both strain release and aromaticity loss simultaneously occur at the reacting bond of the fullerene during reaction (Figure 1) and can be monitored from the $NICS_2$ values and pyramidalization angles (θ) given in Table 4. Hence, these two processes are seemingly competing along with the already existing local strain and aromaticity in the cluster. In principle, the strain will have less impact on the kinetic aspect of a reaction,[23e,f,29] and thus the whole strain on C_{60} seems to be overwhelmed by its global aromaticity, as can be seen from the relative barriers between fullerene and ethylene reactions (Tables 1 and 3). The overall aromaticity of TSs and products found for both reactions clearly indicate this effect from MSE (Tables 1 and 3), showing their large and low values of former and latter reactions, respectively. This is confirmed by our recent studies[11] in which it is proven that the aromatization as well as the aromatic ring function of reactants appreciably enhance the Diels−Alder activity. Also, this is supported by the fact that the cyclic delocalization existing in the TS[11,18,20] clearly distinguishes the TS and product in ethylene reactions, but their aromaticity is almost the same in fullerene reactions as a result of the excess aromaticity in the cluster. In contrast, the exothermicity of fullerene reactions is unexpectedly smaller than the prototype reactions as shown by the reaction energies. Though the strain relief in fullerene appears to facilitate these reactions from the thermodynamic point of view, the aromaticity lost in it considerably reduces the exothermicity of the reactions. However, these processes do not affect the barriers at all. Thus, the efficiency of fullerenes toward Diels−Alder reactions can be related to the effect of aromaticity, and this may be of great interest to fullerene chemists.

Aromaticity Resistance and Its Push−Pull Effect in QDM-C_{60} Reactions. The annelation of various aromatic cycles attached to the cycloadduct of C_{60} occurs in a series of QDM (**A**−**F**)−fullerene reactions through the effect of aromatic stabilization in a diene ring function. Subsequently, these reactions exhibit aromatic destabilization in the two rings of C_{60} joined by the reacting bond. Therefore, aromaticity is progressively gained in QDM as a result of a π-bond formation (2−3, Figure 1) in the reaction, while it is lost in the fullerene as a result of a π-bond cleavage (5−6). This can be evidenced from the $NICS_1$ and $NICS_2$ values given in Table 4; the diatropic shift is thereby increased from R to P through TS in the former case and decreased in the latter. These two simultaneous processes thus reflect their aromaticity effect in an opposite manner. These opposing processes are diminished upon reaction when nucleophilic QDM transmits its gained aromaticity to the electrophilic and aromatic fullerene, thereby strengthening the overall aromaticity. In this context, aromaticity can be considered to be "pushed" by the nucleophilic QDM and "pulled" by a giant aromatic electrophile, the fullerene; these reactions thus generate cycloadducts by a "push−pull aromaticity" process. The MSE and energetics of the reaction will allow us to judge the net result of these effects.

Calculated activation and reaction energies listed in Table 3 show that the reactions for **A** and **C**−**F** are relatively faster and more exothermic than the BD-C_{60} reaction. This is due to the aromatization process occurring in the former reactions, increasing the aromaticity of their TSs and products as compared to the latter case. The "early"/"late" nature of the TSs predicted here is also

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expected in this context. The MSEs of TS and product (Λ_{TS} and Λ_P) indicate that they are indeed higher in the QDM reactions than in the BD reaction. Although the reaction between **B** and the fullerene attains some aromaticity via the benzene ring, its aromaticity is reduced by the oxygen lone-pair repulsion during reaction, and hence this reaction is less favorable than other QDM−fullerene cycloadditions as confirmed by the reaction energetics and MSEs (Table 3). Calculated MSE values further predict that the extent of aromatization in the reaction of **A**, **C**, and **D** with C_{60} is relatively more preferred than that in the reaction involving **E** and **F** as expected on the basis of by the aromaticity of the concerned reference systems.[25] On this basis, one can also anticipate that the aromaticity resistance is lower while its push−pull activity is higher in the former cases than in the latter and that this variation is dependent upon the relative extent of aromatization. The relative energies in Table 3 show that the increased aromaticity in the first set of reactions enhances both the reaction rate and the exothermicity relative to the second set. The extent of aromatization in the **D**−C_{60} reaction slightly exceeds the **C**−C_{60} case because the delocalization is slightly more favored by the symmetric pyrazine function of **D** rather than the asymmetric pyrimidine ring of **C**. The differential preference of aromatization is reflected the MSE values. The former process is kinetically as well as thermodynamically favorable, as can be seen from the energetics. Between the **E**− and **F**−fullerene reactions, the thiophene aromatic stabilization in the former cycloaddition is expected[25] to be more favored than the furan stabilization in the latter case. This is clearly seen in the relative energies and also in MSEs (Table 3). The sum of the results emphasizes the fact that a high degree of aromatization in the QDM−C_{60} reaction involves a greater push−pull aromaticity by reducing as much as possible the aromaticity resistance, thereby enhancing the reaction more efficiently via an “early” TS.

4. Conclusions

The present paper deals with the Diels−Alder reactions of various QDMs with C_{60} using AM1 and high level computations and discusses the reactivity of both reactants through different aromaticity effects. All these reactions proceed via concerted TSs to yield a variety of aromatized fullerene-based adducts. Calculations reveal that the strained olefin of C_{60} is electrophilically much more reactive than the free olefin, ethylene; the numerous aromatic rings in the fullerene globally surmount the influence of net pyramidalization and decrease the barrier. Further, the QDM−C_{60} reactions are all extremely faster and exothermically much favorable than the BD−C_{60} reaction through the influence of aromatic stabilization occurring in the QDM ring function. Besides this aromatization, an aromatic destablization also exists simultaneously at the fullerene reacting junction, reflecting their opposing activity in the reaction. The NICS values provide strong evidence for this progressive aromaticity gain and loss in the reaction. The gained aromaticity in QDM is nucleophilically transferred to a bulk aromatic fullerene in a push−pull way thus canceling the resisting aromaticity. However, a global aromaticity effect emerging from both aromatization and the aromaticity in C_{60} greatly enhances the feasibility of the QDM−fullerene reaction. The net aromaticity of ground and transition state structures obtained from MSE support this aspect. Overall, the results establish the fact that the extent of aromatization increases with increasing reaction rate and exothermicity; the push−pull aromaticity is thereby increased by minimizing the aromaticity resistance.

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