

Diels–Alder [4+2] Cycloadditions of C₂₀ with Some Diene and 1,2-Dioxo Compounds: A Theoretical Study

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Abstract

Diels–Alder [2+4] cycloaddition products of the reaction between C₂₀ and C₄H₄X₂ or C₂O₂X₂ (X = H, F, Cl, CH₃, NH₂, NO₂, and OH) were studied at B3LYP level of theory with 6-31G, 6-31G(d, p) and 6-311G(d, p) basis sets. The HOMO–LUMO gaps of Kohn–Sham orbitals for most of the adducts show evident increase compared with the gap value of C₂₀, suggestive of more stability in the adducts. The thermodynamic calculations indicate that the reaction of diene with C₂₀ is exothermic and spontaneous. While, the addition of 1,2-dioxos to C₂₀ can be thermodynamically improper when the 1,2-dioxo group consists of electronegative atoms.

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1. Introduction

The C₂₀ cage, the smallest and truly unique member of the fullerene family, had been only a theoretical molecule until anion-photoelectron spectroscopy [1] and first-principle calculation [2] showed its existence in vapor phase. Also theoretical studies showed that the C₂₀ cage can also form condensed phases in several dimensions and

the most stable phase is a simple-cubic-like phase with a metallic property [3].

The C₂₀ has been proposed as a possible intermediate to C₆₀ or larger fullerenes [4]. There has been considerable theoretical and experimental interest in the structure of the C₂₀ [5-8].

The geometry of fullerenes obeys the isolated-pentagon rule, which states that the most stable fullerenes are those in which all pentagons located as far as possible from one another and are

surrounded by five hexagons [9]. However, it is impossible to satisfy this rule for the smallest possible fullerene, C_{20} , which contains only 12 pentagons. This implies that this fullerene should be highly reactive owing to the fusion of the strained 5-membered rings and somewhat different reaction behavior of the C_{20} cage is expected.

As the C_{20} cage would be one of the candidates for molecular devices, modification of the structural and electronic properties of C_{20} should be a subject of general interest to both experimentalists and theoreticians. Therefore, Functional fullerenes are expected to have potential applications in biology, materials and other fields. Then, an enormous effort has been dedicated to their chemical functionalization. Although a number of synthetic methodologies have been devised, cycloaddition reactions has been found to offer the most versatile routes for the functionalization of the C_{60} fullerene [10-14].

Despite the huge amount of work devoted to the preparation of fullerene cycloadducts, much less is known however about their chemical and thermal stability. The thermal stability of chemically modified fullerenes is a fundamental aspect in order to determine the best candidates to prepare functional fullerene-based materials able to withstand the ambient conditions to maintain their efficiency, thus preventing any further chemical or thermal degradation [15-17].

The adducts of the most stable fullerene C_{20} isomers with C_2H_2 and C_2H_4 have been studied by the B3LYP method [18]. The derivatives $C_{20}(C_2H_2)_n$ and $C_{20}(C_2H_4)_n$ ($n = 1-3$) exhibit remarkable aromaticity, while $C_{20}(C_2H_2)_3$ and $C_{20}(C_2H_2)_4$ have no spherical aromaticity.

Prior calculations using MP2 methods for smaller systems have shown that for carbon clusters the

convergence of perturbation theory is slow, with reliability of the order of 50 kcal/mole [19].

In the present study, a theoretical investigation has been carried out on [2+4] cycloaddition reactions of $C_4H_4X_2$ and $C_2O_2X_2$ ($X = H, F, Cl, CH_3, NH_2, NO_2, \text{ and } OH$) to C_{20} molecule.

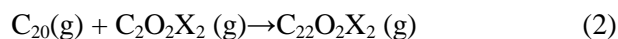


Figure 1 displays the ground-state geometries of $C_{24}H_2X_2$ and $C_{22}O_2X_2$ molecules. Relative stability and the reaction activity of the C_{20} toward the addition of a diene or 1,2-dioxo compounds have been studied.

2. Computational details

The computational procedures started with geometry optimization of an isolated molecule using DFT methods with popular hybrid exchange-correlation functional, B3LYP, with 6-31G, 6-31G(d, p) and 6-311G(d, p) basis sets. Also, the vibrational frequencies analysis were carried out at the same level to analyze the relative energies of the compounds and to assure that the final optimized structures give no imaginary frequencies. For all computations, GAUSSIAN 98 software package has been used [20].

In order to have insight to their reactivity, the relevant frontier molecular orbitals were examined.

3. Results and discussion

All calculations conclude that the ground states of the C_{20} fullerene should have D_{2h} structures. Optimization of the C_{20} fullerene at B3LYP/6-311G(d, p) level of theory shows that the C–C bond length varies from 1.402 to 1.518 Å.

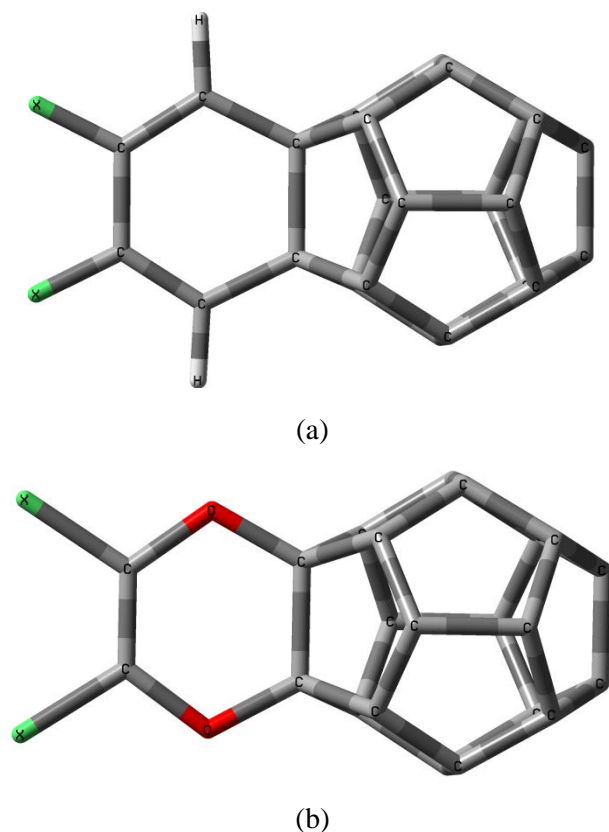


Figure 1. The structures of (a) $C_{24}H_2X_2$, (b) $C_{22}O_2X_2$

The electronic characteristics determining the reactivity of the compounds directly are the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) maps and energies and their difference, the HOMO-LUMO gap abbreviated as HLG. Total Energy, thermal energy, zero point energy (ZPE), HLG and entropy of $C_{24}H_2X_2$ and $C_{22}O_2X_2$ using of B3LYP method with different Basis sets at 298 K are collected in Table 1.

The adducts of the C_{20} with $C_4H_4X_2$ are named A1, A2, A3, A4, A5, A6 and A7 for $X = H, CH_3, F, Cl, NH_2, OH$ and NO_2 , respectively. Similarly, the adducts of the C_{20} with $C_2O_2X_2$ are named B1, B2, B3, B4, B5, B6 and B7 for $X = H, CH_3, F, Cl, NH_2, OH$ and NO_2 , respectively.

As can be seen from Table 1, addition of polarized basis functions affects all parameters. Furthermore, the following trends with basis set can be deduced for the entropy of each compound.

$$6-31G(d,p) > 6-311G(d,p) > 6-31G$$

The HOMO-LUMO gap is traditionally associated with chemical stability against electronic excitation; the larger gap corresponds to greater stability. The HOMO-LUMO gaps of Kohn-Sham orbitals calculated at B3LYP level for the adducts show evident increase compared to the gap value of C_{20} , 1.940 eV (except for B6 with 6-311G(d, p) and 6-31G basis sets and B5 with 6-31G basis set), suggestive of more stability in the adducts. The B6 structure optimized at the B3LYP/6-311G(d, p) level was found to be unstable with three imaginary frequencies. Analysis of the frequency of other compounds shows that they are stable without any imaginary frequency.

The graphical representations of the HOMO and LUMO orbitals of $C_{24}H_2X_2$ and $C_{22}O_2X_2$ at the level of B3LYP/6-311G(d, p) are shown in Figure 2. Figure 2 clearly illustrates the frontier orbital populations of these derivatives.

It is seen that the HOMO and LUMO maps in A-molecules are approximately equivalent and have distribution on the C_{20} cage while the HOMO orbitals of B molecules have different contribution of the C_{20} cage and the additive part. The HOMO orbitals mainly distribute on the additive part of B-molecules and imply that these sites are probably the most reactive sites.

In order to investigate the performance of reactions 1 and 2, the enthalpy and the Gibbs free energy for each reaction was calculated.

Table 1. Total Energy, thermal energy, zero point energy and entropy of C₂₄H₂X₂ and C₂₂O₂X₂ using of B3LYP method with different Basis sets at 298 K

| Mol. | Total Energy (hartree) | E _{Thermal} (Kcal/mol) | ZPE (Kcal/mol) | S (cal/molK) | HLG (eV) | Mol. | Total Energy (hartree) | E _{Thermal} (Kcal/mol) | ZPE (Kcal/mol) | S (cal/molK) | HLG (eV) |
|--------------------|------------------------|---------------------------------|----------------|--------------|----------|--------------------|------------------------|---------------------------------|----------------|--------------|----------|
| 6-31G | | | | | | 6-31G | | | | | |
| A1 | -916.080 | 123.243 | 116.815 | 98.745 | 2.463 | B1 | -989.043 | 106.828 | 100.2593 | 103.697 | 2.561 |
| A2 | -994.698 | 160.475 | 152.068 | 112.725 | 2.471 | B2 | -1067.669 | 143.952 | 135.3336 | 115.298 | 2.514 |
| A3 | -1114.497 | 113.721 | 106.133 | 107.877 | 2.460 | B3 | -1187.449 | 97.299 | 89.7311 | 108.016 | 2.517 |
| A4 | -1835.220 | 112.404 | 104.345 | 113.077 | 2.449 | B4 | -1908.174 | 95.796 | 87.7331 | 113.445 | 2.512 |
| A5 | -1026.759 | 146.390 | 138.218 | 110.686 | 2.484 | B5 | -1099.723 | 129.574 | 121.1649 | 112.544 | 1.769 |
| A6 | -1066.455 | 129.417 | 121.523 | 109.213 | 2.476 | B6 | -1139.414 | 112.544 | 104.2987 | 112.033 | 1.924 |
| A7 | -1324.890 | 128.120 | 118.324 | 126.429 | 2.411 | B7 | -1397.764 | 110.287 | 100.5809 | 123.791 | 2.427 |
| 6-31G(d,p) | | | | | | 6-31G(d,p) | | | | | |
| A1 | -916.357 | 122.684 | 116.056 | 99.771 | 2.664 | B1 | -989.363 | 106.341 | 100.2321 | 96.352 | 2.767 |
| A2 | -994.999 | 159.620 | 151.006 | 113.817 | 2.667 | B2 | -1068.007 | 141.819 | 134.4155 | 105.230 | 2.449 |
| A3 | -1114.814 | 113.497 | 105.754 | 108.632 | 2.669 | B3 | -1187.814 | 97.771 | 90.1321 | 108.201 | 2.721 |
| A4 | -1835.538 | 112.108 | 103.907 | 113.709 | 2.653 | B4 | -1908.540 | 96.181 | 88.06756 | 113.390 | 2.713 |
| A5 | -1027.078 | 145.806 | 137.511 | 111.298 | 2.688 | B5 | -1100.084 | 129.762 | 121.4602 | 111.679 | 2.191 |
| A6 | -1066.796 | 129.577 | 121.481 | 110.298 | 2.686 | B6 | -1139.799 | 113.442 | 105.1998 | 111.501 | 2.161 |
| A7 | -1325.334 | 128.777 | 118.855 | 126.966 | 2.615 | B7 | -1398.236 | 111.504 | 101.8991 | 122.779 | 2.542 |
| 6-311G(d,p) | | | | | | 6-311G(d,p) | | | | | |
| A1 | -916.537 | 122.343 | 115.762 | 99.504 | 2.640 | B1 | -989.567 | 105.962 | 99.8890 | 96.159 | 2.746 |
| A2 | -995.193 | 159.030 | 150.444 | 113.720 | 2.642 | B2 | -1068.226 | 143.010 | 134.324 | 115.204 | 2.550 |
| A3 | -1115.059 | 113.180 | 105.497 | 108.297 | 2.642 | B3 | -1188.079 | 96.959 | 89.8178 | 103.961 | 2.449 |
| A4 | -1835.772 | 111.806 | 103.645 | 113.505 | 2.629 | B4 | -1908.797 | 95.854 | 87.7769 | 113.160 | 2.691 |
| A5 | -1027.287 | 145.395 | 137.136 | 111.108 | 2.661 | B5 | -1100.318 | 129.344 | 121.0713 | 111.514 | 2.106 |
| A6 | -1067.022 | 129.255 | 121.196 | 110.102 | 2.659 | B6 | -1140.042 | 111.397 | 104.1991 | 104.160 | 1.567 |
| A7 | -1325.627 | 128.389 | 118.501 | 126.854 | 2.596 | B7 | -1398.547 | 111.154 | 101.5991 | 122.458 | 2.430 |

The corresponding heat of reaction ΔH_{298} can be calculated using the following expression:

$$\Delta H_{298} = \Delta E + \Delta(PV) = \Delta E_0 + \Delta ZPE + \Delta H_T + \Delta nRT \quad (3)$$

where ΔE_0 is the change in total energy between the products and the reactants at 0 K, ΔZPE is the difference between the zero-point energies (ZPE) of the products and the reactants, ΔH_T is thermal correction from 0 to 298 K and $\Delta(PV)$ value is the PV work term which equals ΔnRT . $\Delta S_{r,298}$ and $\Delta G_{r,298}$ are entropy and Gibbs free energy difference between products and the reactants at 298 K.

Table 2 shows thermodynamic properties of reactions 1 and 2. The Calculated ΔH_{298} and ΔG_{298} at B3LYP level are negative for A1-A7 compounds which show that all reactions are exothermic and spontaneous. While The Calculated ΔH_{298} for B1-B7 is negative but the decrease of the entropy results a positive ΔG_{298} for some of B-molecules when X is an electron acceptor group. The results of table 2 indicate the important effect of the basis set on the calculation of thermodynamic properties So, ΔG_{298} increases from 6-31G basis set to 6-311G(d, p) basis set.

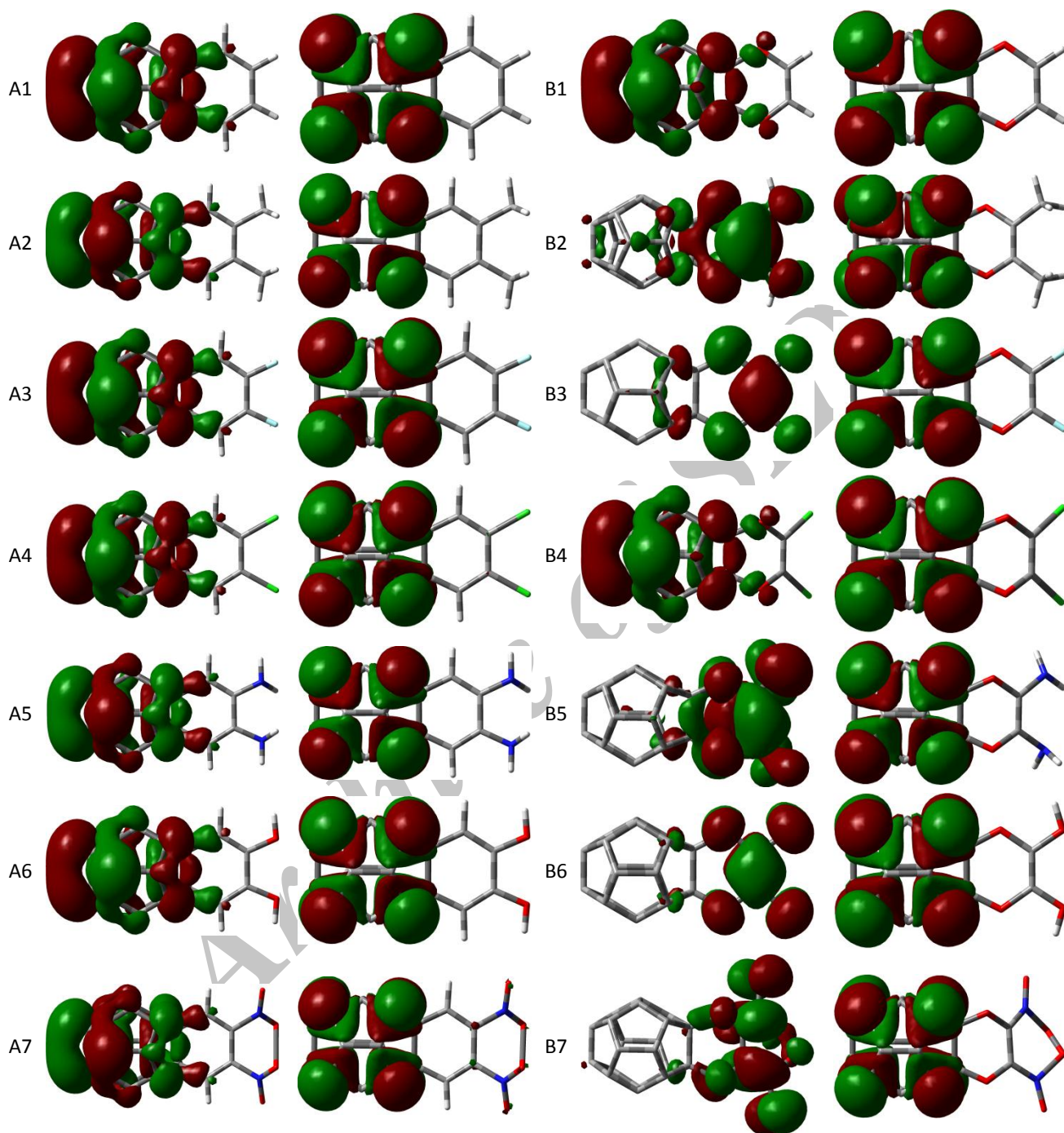


Figure 2. The atomic structures, HOMOs, and LUMOs of $C_{24}H_2X_2$ and $C_{22}O_2X_2$ at the level of B3LYP/6-311G(d, p).

Table 2. Thermodynamic parameters of $C_{24}H_2X_2$ and $C_{22}O_2X_2$ using of B3LYP method with different Basis sets at 298 K (in Kcal/mole)

| Mol. | ΔE | ΔH | ΔS | ΔG | Mol. | ΔE | ΔH | ΔS | ΔG |
|--------------------|------------|------------|------------|------------|--------------------|------------|------------|------------|------------|
| 6-31G | | | | | 6-31G | | | | |
| A1 | -62.7779 | -62.7779 | -0.0250 | -55.3158 | B1 | -52.6476 | -53.2400 | -0.0497 | -38.4163 |
| A2 | -67.3619 | -67.3619 | -0.0228 | -60.5796 | B2 | -44.1161 | -44.7085 | -0.0519 | -29.2241 |
| A3 | -57.7661 | -57.7661 | -0.0250 | -50.3160 | B3 | -24.5878 | -25.1802 | -0.0552 | -8.7250 |
| A4 | -59.3074 | -59.3074 | -0.0253 | -51.7609 | B4 | -31.1837 | -31.7761 | -0.0559 | -15.1214 |
| A5 | -67.3619 | -67.3619 | -0.0228 | -60.5796 | B5 | -7.23074 | -7.82314 | -0.0503 | 7.1705 |
| A6 | -61.8522 | -61.8522 | -0.0238 | -54.7630 | B6 | -17.3419 | -17.9343 | -0.0504 | -2.8950 |
| A7 | -60.3876 | -60.3876 | -0.0114 | -57.0001 | B7 | -13.1419 | -13.7343 | -0.0467 | 0.1932 |
| 6-31G(d,p) | | | | | 6-31G(d,p) | | | | |
| A1 | -60.4716 | -60.4716 | -0.0297 | -51.6068 | B1 | -50.6213 | -51.2137 | -0.0630 | -32.4389 |
| A2 | -64.7720 | -64.7720 | -0.0274 | -56.5988 | B2 | -41.3470 | -41.9394 | -0.0680 | -21.6581 |
| A3 | -56.9814 | -56.9814 | -0.0296 | -48.1490 | B3 | -19.0857 | -19.6781 | -0.0606 | -1.6069 |
| A4 | -59.1032 | -59.1032 | -0.0298 | -50.2055 | B4 | -29.9226 | -30.5150 | -0.0613 | -12.2307 |
| A5 | -65.5024 | -65.5024 | -0.0264 | -57.6352 | B5 | -7.56584 | -8.15824 | -0.0587 | 9.3306 |
| A6 | -60.4584 | -60.4584 | -0.0285 | -51.9506 | B6 | -11.5323 | -12.1247 | -0.0564 | 4.7020 |
| A7 | -61.0491 | -61.0491 | -0.0163 | -56.1795 | B7 | 3.1215 | 2.5291 | -0.0533 | 18.4298 |
| 6-311G(d,p) | | | | | 6-311G(d,p) | | | | |
| A1 | -57.8945 | -57.8945 | -0.0274 | -49.7362 | B1 | -45.4302 | -46.0226 | -0.0606 | -27.9657 |
| A2 | -62.1234 | -62.1234 | -0.0250 | -54.6651 | B2 | -42.4547 | -43.0471 | -0.0555 | -26.4891 |
| A3 | -54.0162 | -54.0162 | -0.0273 | -45.8913 | B3 | -11.6872 | -12.2796 | -0.0622 | 6.2543 |
| A4 | -56.1897 | -56.1897 | -0.0274 | -48.0097 | B4 | -23.9053 | -24.4977 | -0.0591 | -6.8898 |
| A5 | -62.2312 | -62.2312 | -0.0241 | -55.0604 | B5 | -1.9566 | -2.5490 | -0.0560 | 14.1552 |
| A6 | -57.3786 | -57.3786 | -0.0260 | -49.6282 | B6 | -4.4108 | -5.0032 | -0.0611 | 13.2194 |
| A7 | -58.3663 | -58.3663 | -0.0139 | -54.2148 | B7 | 14.1886 | 13.5962 | -0.0513 | 28.8889 |

4. Conclusion

The structures and stabilities of fullerenes C_{20} and some of its derivatives have been studied by DFT calculations. The calculations show that the fullerene C_{20} has a high activity toward addition of diene or 1,2-dioxo and the adducts have high stabilities relative to C_{20} except for $C_{22}O_2(OH)_2$. The thermodynamic calculations indicate that the reaction of the addition of diene to C_{20} is exothermic and spontaneous. While, the addition of 1,2-dioxos to C_{20} can be thermodynamically improper when the 1,2-dioxo group consists of electronegative atoms.

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