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Fullerene compounds with general formulae $C_{60}O_x$ (x = 1–3): isomerism, stability and polarizability

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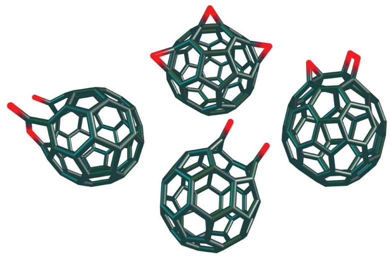
The trends of stability and polarizability have been computationally deduced for the sets of oxygen-containing fullerene derivatives $C_{60}O$, $C_{60}O_2$ and $C_{60}O_3$ (2, 11 and 68 isomers, respectively).



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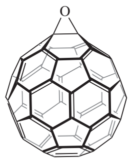
Oxidation of fullerenes with diverse oxidants (oxygen and its active forms, ozone, peroxide compounds, *etc*.) has been studied for more than 30 years (see, *e.g.*, reviews[1,2]). Currently, the following oxygen-containing fullerene derivatives $C_{60}O_x$ are experimentally known (detected or detected and structurally characterized): epoxides $C_{60}O_x$ (x = 1–6),[3] unstable oxidoannulene $C_{60}O$,[4] primary ozonides $C_{60}(O_3)_{1-2}$ and epoxy ozonides $C_{60}(O)O_3$,[5] open-cage ketones $C_{60}O_z$[3] and keto lactone $C_{60}O_3$.[6] There is an experimental evidence for the formation of dioxetane $C_{60}O_2$,[7] one-cage $C_{60}O_3$ and double-cage $(O{=}C_{60})_2O_3$ secondary ozonides.[8] The diversity of the fullerene–oxygen molecular species becomes higher if we also take into account labile intermediates of the oxidation processes, *e.g.*, open-cage carbonyl oxides[9] and π-complex $C_{60}\cdots O_3$[10] formed upon the fullerene ozonolysis. Additionally, there are entirely hypothetical fullerene–oxygen compounds such as polyepoxides $C_{60}O_x$ (with x up to 30)[11] or endohedral complex $O_3@C_{60}$.[12]

Fullerene–oxygen species are highly likely products of C_{60} transformations under environmental and interstellar conditions.[13] Analysis of such environmental compositions is experimentally very hard, so it is usually complemented with relevant theoretical estimates. The possibility of forming these or those isomers $C_{60}O_x$ can be estimated within minimum-energy and minimum-polarizability principles.[14,†]

In the present work, we have computed the total energies and mean polarizabilities of isomeric O-containing derivatives $C_{60}O_x$ (x = 1–3) with the PBE/3ζ density functional theory method.[‡] The stabilities within each series $C_{60}O$, $C_{60}O_2$ and $C_{60}O_3$ were estimated as the energy effects ΔE_r of the formal chemical equation:[§]

$$C_{60} + \tfrac{x}{2}O_2 \rightarrow C_{60}O_x . \qquad (1)$$

We focus on the C_{60} derivatives functionalized *via* 6,6 bond of the fullerene core due to their higher thermodynamic favorability as compared with 5,6 bond derivatives.[2,4,11] Our present calculations reproduce this known tendency in a pair of $C_{60}O$ structural isomers, *viz*. 6,6-closed epoxide **1** (more stable and less polarizable) and 5,6-open oxidoannulene **2** (*vice versa*)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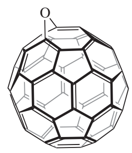
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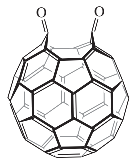
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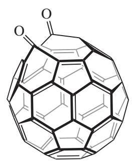
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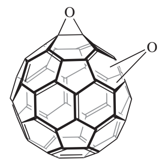
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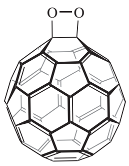
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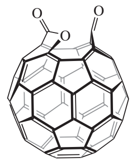
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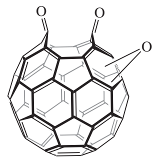
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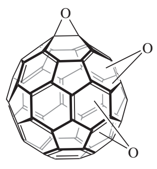
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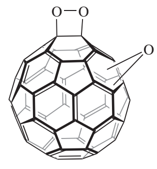
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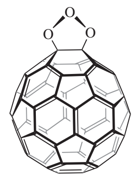
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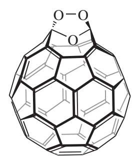
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(Table 1).[‡] In the case of the $C_{60}O_2$ isomers, the stability of the compounds decreases in the series: *cis*-1-diepoxide > 6,6-open diketone > other isomeric diepoxides > 5,6-open diketone > *cis*-

† Minimum polarizability principle states that the most stable isomer has the least mean polarizability as compared with other compounds of the isomeric set. Note that the principle has a quality of correlation and some compounds do not obey it.[15]

‡ The quantum chemical calculations were performed by the PBE/3ζ method (Priroda 6.0 program[16]), which correctly reproduces structures and energetic properties of fullerenes and their derivatives.[10,11,14,17] Mean polarizabilities were calculated using the finite-field approach. All mean polarizabilities within the regioisomeric series are given in Online Supplementary Materials.

§ The calculated energy estimates include zero-point vibration energies. Dioxygen is in the triplet state.

Table 1 The energetic effects of reactions (1) and mean polarizabilities of the formed oxygen-containing fullerene derivatives.

$C_{60}O_x$	Number of regio-isomers	ΔE/kJ mol^{-1}	α/Å^3
$C_{60}O$, epoxide **1**	1	–57.7	83.25
$C_{60}O$, oxidoannulene **2**	1	–55.6	83.85
$C_{60}O_2$, 6,6-open diketone **3**	1	–129.6	86.11
$C_{60}O_2$, 5,6-open diketone **4**	1	–107.0	86.89
$C_{60}O_2$, diepoxides **5**	8	–133.4…–108.7	83.64–83.80
$C_{60}O_2$, dioxetane **6**	1	+9.0	84.60
$C_{60}O_3$, keto lactone **7**	1	–360.7	87.34
$C_{60}O_3$, epoxy diketones **8**	9	–220.0…–175.5	86.35–86.75
$C_{60}O_3$, triepoxides **9**	45	–216.8…–146.3	84.03–84.11
$C_{60}O_3$, epoxy dioxetanes **10**	9	–71.8…–40.2	84.92–85.22
$C_{60}O_3$, primary ozonide **11**	1	–5.6	85.85
$C_{60}O_3$, secondary ozonide **12**	1	+200.5	86.32

2-diepoxide > dioxetane (see Table 1). Herewith, the formation of the latter structure **6** is endothermic and there is only one evidence of its reversible formation.[7] *cis*-1-Diepoxide and diketone **3** are the most stable compounds with a wide margin. At the same time, diketone **3** is the most polarizable compound of the $C_{60}O_2$ set (due to the conjugation of two C=O groups with the modified π-electronic system of the fullerene core), so the minimum-polarizability principle[15] is violated.

We included 5,6-open diketone **4** to the set. It has been entirely hypothetical compound for a long time[18] until Tabari and Farmanzadeh[19] have computationally found it as a product of reaction $\mathbf{2} + O_3 \rightarrow \mathbf{4} + O_2$. Here we note that diketone **4** is ~20 kJ mol^{-1} less stable than diketone **3** but more favorable than the least stable *cis*-2-diepoxide.

The stability of the $C_{60}O_3$ isomers decreases as follows: keto lactone **7** > epoxy diketones **8** and triepoxides **9** > epoxy dioxetanes **10** > primary ozonide **11** > secondary ozonide **12**. Keto lactone **7** is the unattainable leader in this set (~140 kJ mol^{-1} gap between **7** and next stable $C_{60}O_3$). These calculations correspond to the Bulgakov *et al.* works,[3] whereby such oxygen functional groups are found typical of deeply ozonized C_{60}. As in the case above, the minimum polarizability principle is violated as the most stable compound (**7**) is simultaneously the most polarizable.

Ozonides are the least stable $C_{60}O_3$ isomers. Notably, the synthesized[5] primary ozonide **11** has the smallest exothermic effect whereas highly endothermic reaction (1) corresponds to the secondary ozonide **12**, whose formation is a big question.[8]

There is common regularity in the stability of the regioisomeric bis-adducts **5**, **8** and **10**. Among these C_{60} derivatives, *cis*-1 and *cis*-2 isomers are more stable and least stable, respectively. In general, exothermicity of $C_{60}O_x$ formation increases from $x = 1$ to $x = 3$ for oxy derivatives with similar functional groups, *e.g.*, in the case of the fullerene epoxides ($\mathbf{1} < \mathbf{5} < \mathbf{9}$). This trend makes initially endothermic reactions more favorable. Indeed, formation of dioxetanes **8** from epoxide $C_{60}O$ becomes exothermic in contrast to the formation of dioxetane **6** from the pristine fullerene.

To complete the $C_{60}O_3$ picture, we consider two isomeric molecular complexes $O_3\cdots C_{60}$ (indirectly evidenced in experiment) and $O_3@C_{60}$ (currently hypothetical) with ozone molecules outside and inside the cage, respectively. Such topological isomerism based on opposition *exo–endo* has been first predicted by V. I. Sokolov[20], however, it was scarcely exemplified. The stability of complexes $O_3\cdots C_{60}$[10] and $O_3@C_{60}$[12] has been previously studied and here we stress the drastic difference in their polarizability. The calculated mean polarizabilities of $O_3\cdots C_{60}$ and $O_3@C_{60}$ are 93.48 and 84.06 Å^3. Their deviations $\Delta\alpha$ from the relevant additive scheme[¶] make up +8.38 and –1.04 Å^3, respectively. It is noteworthy that $\Delta\alpha$ values differ by sign. In the case of endohedral $O_3@C_{60}$, $\Delta\alpha < 0$ indicates the dielectric screening of the ozone by the fullerene cage (similar to other endohedral complexes of C_{60})[21] whereas $\Delta\alpha > 0$ for $O_3\cdots C_{60}$ reflects mutual polarization of the electronic clouds of C_{60} and O_3 upon complexation.

To sum up, within the series of the studied $C_{60}O_x$ compounds, the trends of the energy and polarizability do not coincide as would expected from the minimum polarizability principle. As these quantities are decisive for the abundances of chemical substances in various media,[14] they should be jointly applied to predicting the most probable candidates for detecting in natural environment.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.01.030.

¶ $\Delta\alpha = \alpha(\text{complex}) - [\alpha(C_{60}) + \alpha(O_3)]$, where the brackets contain the additive value equal to the sum of the mean polarizabilities of the isolated molecules. According to the PBE/3ζ method, $\alpha(C_{60}) = 82.7$ and $\alpha(O_3) = 2.4$ Å^3.

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