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Ozonolysis of polycyclic aromatic hydrocarbons in participating solvents†

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Seven polycyclic aromatic hydrocarbon (PAH) compounds that can be considered small models for graphene edges have been treated with ozone in solution. The presence of participating solvents such as water or methanol had a pronounced influence on conversion and identity of the functional groups formed, whereas the regioselectivity of the ozonation remained unaffected. Six previously unreported compounds have been isolated from the ozonolysis of pyrene **1**, perylene **2** and benzo[*e*]pyrene **4**. Comparison of the experimental data with calculated local ionization energy surfaces (IES) shows a good correlation, and indicates that this computational tool would be useful to predict the regioselectivity of ozone also for larger PAHs, including graphene and graphene nanoribbons.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) constitute a group of compounds of interest in many different fields such as organic dyes, ligands for asymmetric catalysis, pharmaceuticals, agrochemicals and have the potential to be used as both organic conductors or semiconductors,^{1–3} but also as models for graphene and graphene nanoribbons (GNRs).⁴ In previous work in our group, graphene on graphite and graphene on SiC was treated with ozone under dry and aqueous conditions, and an edge selectivity for the reaction is observed with introduction of ether/phenolic components and ester/carboxylic groups, leaving the bulk of the material unchanged.^{5–7} Calculations show that the differences in thermodynamic reactivity between the edges and the internal plane for graphene for cycloaddition reactions are large, with reaction at internal positions leading to significantly less stable states than reaction at edge positions.^{8,9}

PAHs are constructed of sp² hybridized carbons in fused aromatic motifs, and can therefore be referred to as the smallest and most well-defined members of the nanographene family. Several graphene edge motifs are readily available (Chart 1), which opens for studies of structure-related reactivity and regioselectivity using soluble models.

In organic synthesis, ozone is used for oxidative cleavage (ozonolysis) of alkenes.¹⁰ Ozonation of PAHs, has been studied in the context of oxidative degradation in the environment,¹¹ but also in a more synthetic perspective.^{12,13} Reactions between ozone and PAHs display regioselectivity as well as position-dependent variations in which functional groups that are formed.^{14–17} Extrapolating these observations to hydrogen-

terminated graphene and graphene nanoribbons (GNRs) indicates a great potential for selective edge functionalizations leading to chemical differentiation of graphene edges. Selective functionalization of graphene is of interest both from a fundamental perspective as well as for application development.^{18,19}

In order to evaluate and rationalize the influence of the edge structure¹ seven different PAHs were chosen; pyrene (**1**), perylene (**2**), benzo[*a*]pyrene (B[*a*]P, **3**), benzo[*e*]pyrene (B[*e*]P, **4**), triphenylene (**5**), acenaphthylene (**6**) and anthracene (**7**) (Chart 1). Between them, PAHs **1–7** represent the most common edge motifs for graphene,²⁰ namely; *k* region (armchair), bay region (armchair), zigzag region and five ring defect, in different combinations. Pyrene **1** has *k* regions, perylene **2** has zigzag and bay regions, B[*a*]P **3** has zigzag, *k* region and a bay region, B[*e*]P **4** has bay regions and a *k* region, triphenylene **5** has only bay regions, acenaphthylene **6** has a five ring with a localized double bond and anthracene **7** has zigzag edges.

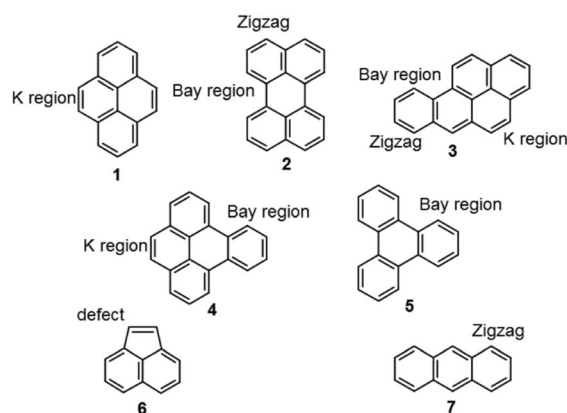


Chart 1 Pyrene (**1**), perylene (**2**), benzo[*a*]pyrene (B[*a*]P, **3**), benzo[*e*]pyrene (B[*e*]P, **4**), triphenylene (**5**), acenaphthylene (**6**) and anthracene (**7**).

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Here, the regioselectivity of the reaction between PAHs and ozone in setups that can be adapted also to suspensions of graphene, the types of functionalities obtained and their dependence on edge structure and participatory solvents are discussed and correlated to calculated local ionization energy surfaces (IES) of the experimentally investigated PAHs.

Materials and methods

Ozone was generated by a corona discharge generator and transported in a dioxygen gas stream to the relevant reaction vessel (2 or 20 mL) *via* Teflon tubing and a stainless steel syringe. All the reactions were performed at 20 °C and the specified reaction time denotes the time that ozone was delivered to the vessel.

Ozonides can undergo thermal decomposition and to minimize the risk, only small scale reactions (≤ 0.1 mmol) were performed and safety guidelines for working with peroxides were followed.²¹ Dichloromethane was used as solvent since it is ozone stable, dissolves PAHs 1–7 well and is a polar aprotic solvent. In the reactions with water as participating solvent, acetonitrile (which is ozone stable) was added to the mixture to support a homogeneous solution. Dichloromethane and methanol are miscible.

The overall conversion of starting material and the conversion to products were determined by analyzing the crude reaction mixtures by quantitative ¹H NMR spectroscopy with 1,2-dichloroethane as internal standard (qNMR). The results reveal the formation of the initial products in the oxidative degeneration pathway for PAHs by ozone, as well as structure related differences in reactivity. The major products for each condition and PAH were isolated using preparative HPLC and structurally determined using NMR spectroscopy and HRMS or, if

previously reported, NMR spectroscopy and MS. The structurally determined products are shown in Chart 2.

Results and discussion

Standard ozonolysis of PAHs

The baseline experimental procedure, without any participating solvents, involved ozonation in dry dichloromethane at 20 °C with no additional reagents during the work up procedure. This gave the mono-ozonides **1a** and **4a** as major products for pyrene **1** and B[*e*]P **4**, both having *k* regions. The ozonolysis of perylene **2** lead to the generation of a black precipitate when the solvent was removed. This black solid was not soluble in any of the attempted solvents and are suspected to be a polymer (poly-ozonide) similar to the polymer that are reported to form upon treating acenaphthylene **6** with ozone.²² No perylene ozonide was detected in the crude reaction mixture (of what was still soluble). The soluble products was isolated using prep HPLC and identified as unsaturated aldehyde **2a**, carboxylic acid **2c** and aldehyde **2b** from cleaving the inside of one of the bay regions.

Triphenylene **5** was the most ozone-stable compound, but with longer reaction times than for the other PAHs, it too was eventually degraded but not to products in amounts detectable by ¹H NMR spectroscopy. For acenaphthylene **6**, a white precipitate formed during the reaction under dry conditions and full conversion was very fast but no products were detected by ¹H NMR spectroscopy. According to literature,²² this white insoluble powder is a polyozonide. With B[*a*]P **3** a mixture of many products was quickly obtained. Since, the ¹H NMR spectrum was very crowded, the crude mixtures were not analyzed by qNMR spectroscopy nor were any major products isolated (see ESI, Fig. S4†). The difficulty of obtaining products in isolatable amount by ozonolysis of B[*a*]P **3** have previously been noted by Fieser²³ though, isolated compounds, mainly different quinones, have been reported in poor yields.^{17,24} Being highly carcinogenic and not providing easily interpreted information, B[*a*]P **3** was removed from further studies. Anthracene **7** was reactive, and almost 90% reacted directly and the only detectable product by ¹H NMR spectroscopy was anthraquinone **7a** in low amounts (15–16%).

Table 1 describes the conditions and results of the dry ozonolysis of selected PAHs for which products were isolated and characterized.

From these results, it can be proposed that when treating defect-free graphene and GNRs with ozone under dry conditions, there will be ozonides on the armchair edges and corners and carbonyls that might tautomerize to phenols on the zigzag edges. In previous study where ozone was reacted with graphite⁵ no ketones were observed, only phenols.

Ozonolysis of PAHs with water as participating solvent

Ozone can decompose in water resulting in a number of reactive oxidative species (*e.g.* radicals).²⁵ Water can also participate in the reaction by trapping the carbonyl oxide intermediate formed during ozonolysis yielding other ozonolysis

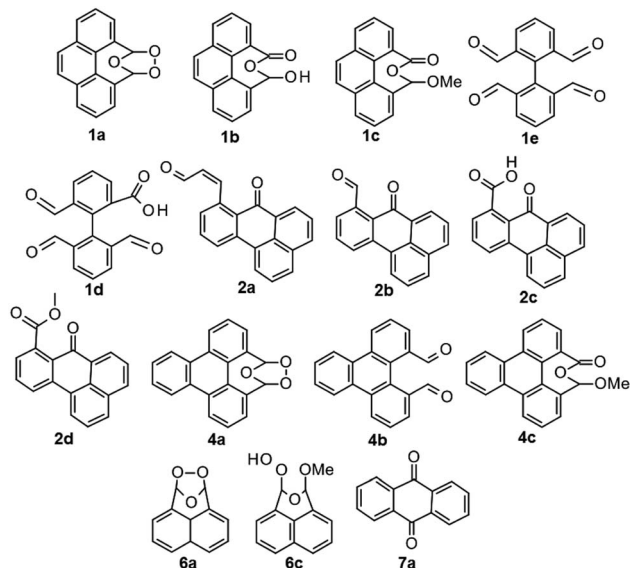


Chart 2 The products from ozonolysis of PAHs **1**, **2**, **4**, **6** and **7** using either water or methanol as participating solvents or under dry conditions in DCM. The previously unreported compounds are **1d**, **2a–d**, **4a**.



Table 1 Ozonolysis of compounds **1–2**, **4–5** in dry DCM (0.025 mmol scale) or dry DCM-d₂ (0.01 mmol scale) at 20 °C. All conversions are from quantitative ¹H NMR spectroscopy with 1,2-DCE as internal standard and the error is 1%

Scale, mmol	V, mL	Ozone time, s	Substrate (conversion of %)	Product (conversion to %)
0.01	2	5	1 (40)	1a (41)
0.025	4	25	1 (80)	1a (77)
0.01/2 ^a	2/2	+5	1 (91)	1a (73)
0.025	4	25	2 (95)	2a (12), 2b (2), 2c (12) + polyozonide
			3	Too many products
0.01	2	5	4 (40)	4a (32)
0.025	4	25	4 (88)	4a (71)
0.01/2 ^a	2/2	+5	4 (98)	4a (73)
0.01	2	15	5 (29)	No detectable ^b product
0.025	4	50	5 (54)	No detectable ^b product
0.01/2 ^a	2/2	+15	5 (63)	No detectable ^b product
			6	Polyozonide
0.01	2	5	7 (88)	7a (15)
0.01	2	+5	7 (90)	7a (16)

^a The 0.01 mmol scale experiments were performed by dissolving 0.01 mmol PAH in 2 mL DCM-d₂, followed by ozone treatment and leaving the sample for 30 min at 20 °C, then half the sample was transferred to a NMR tube and 1,2-DCE was added and half was treated with as much ozone again before it too was transferred to a NMR tube and 1,2-DCE added. ^b No new peaks in the ¹H NMR spectrum.

products such as aldehydes, ketones, carboxylic acids, oxyhydroperoxides than the ozonide.^{10,12,26,27}

With water as the participating solvent the ozonolysis of the PAHs progressed in a similar fashion as without, the ozonide was still the major product with pyrene **1** and B[e]P **4**. From pyrene **1** also the aldehyde **1e**, the carboxylic acid **1d** and the hydroxy ester **1b** are obtained. From B[e]P **4** also the aldehyde **4b** is obtained. From perylene **2** the same products are obtained as for dry conditions, the unsaturated aldehyde **2a**, carboxylic acid **2c** and aldehyde **2b**, and in the same low conversions. The black precipitate was also obtained and again no ozonide was detected in the crude mixture. For B[a]P **3** and triphenylene **5** again no major products were isolated. For perylene **2** and acenaphthylene **6** same results as observed from the experiments at dry conditions were obtained, and precipitates are formed during

the reaction. Anthracene **7** reacted the same way as for under dry conditions, only with a bit lower conversion to **7a**.

Table 2 describes the conditions and results of the ozonolysis of selected PAHs for which products were isolated and characterized when water was used as participating solvent.

Mono-ozonide **1a** has been reported in yields between 23–52%, and the reduced mono-ozonide **1a** (the dialdehyde) in yields of 25–28% from reductive ozonolysis of pyrene **1**.^{28–30} Also tetraaldehyde **1e** has been reported as products from the reductive ozonolysis of pyrene **1**, in yields between 46–55% (ref. 23 and 31–33) using common reductive work-up procedures and very similar ozonolysis procedures as for the mono-ozonide **1a** and dialdehyde synthesis. Unlike the mono-ozonide **1a**, the diozonide from ozonolysis of pyrene **1**, which upon reduction would yield the tetraaldehyde **1e**, is not

Table 2 Ozonolysis of compound **1–2**, **4–6** in DCM : MeCN : water (0.025 mmol scale) or DCM-d₂ : MeCN-d₃ : D₂O (0.01 mmol scale) at 20 °C. All conversions are from quantitative ¹H NMR spectroscopy with 1,2-DCE as internal standard and the error is 1%

Scale, mmol	V, mL	Ozone time, s	Substrate (conversion of %)	Product (conversion to %)
0.01	2	5	1 (35)	1a (22), 1b (11), 1d (<1), 1e (1)
0.025	4	25	1 (85)	1a (37), 1b (15), 1d (3), 1e (5)
0.01/2 ^a	2/2	+5	1 (94)	1a (60), 1b (14), 1d (8), 1e (12)
0.025	4	25	2 (90)	2a (5), 2b (10), 2c (16)
0.01	2	5	4 (36)	4a (21), 4b (0), 4d (8)
0.025	4	25	4 (83)	4a (44), 4b (0), 4d (20)
0.01/2 ^a	2/2	+5	4 (92)	4a (36), 4b (5), 4d (0)
0.01	2	15	5 (24)	No detectable ^b product
0.025	4	50	5 (46)	No detectable ^b product
0.01/2 ^a	2/2	+15	5 (60)	No detectable ^b product
			6	Polyozonide
0.01	2	5	7 (87)	7a (10)
0.01	2	+5	7 (90)	7a (11)

^a The 0.01 mmol scale experiments were performed by dissolving 0.01 mmol PAH in 2 mL DCM-d₂, followed by ozone treatment and leaving the sample for 30 min at 20 °C, then half the sample was transferred to a NMR tube and 1,2-DCE was added and half was treated with as much ozone again before it too was transferred to a NMR tube and 1,2-DCE added. ^b No new peaks in the ¹H NMR spectrum.



to be found in the literature. Surprisingly, in our experiments neither the dialdehyde nor the diozonide from ozonolysis of pyrene **1** was observed in the crude reaction mixture under any conditions. An explanation for this discrepancy was found by Vollman *et al.*,²⁴ who reported that ozonolysis of pyrene during longer times gives the tetraaldehyde **1e** upon reduction and shorter times the aldehyde–carboxylic acid (as **1b**) upon red work up of the mono-ozonide **1a**. Here, no longer times were attempted and all experiments were stopped before 100% conversion of **1**, explaining the lack of dialdehyde and diozonide.

From these results, it can be proposed that when treating defect free graphene and GNRs with ozone and water, there will be ozonides, aldehydes, hydroxy esters and carboxylic acids on the armchair edges and corners and carbonyls that might tautomerize to phenols on the zigzag edges. Ozone can also degrade in water, forming radical oxidative species,²⁵ these radicals can also be expected to react. In this study with ozone and PAHs, no products from degenerated ozone were observed in the crude NMRs (when compared to NMR spectra predicted in MestReNova 8.1.4).

Ozonolysis of PAHs with methanol as participating solvent

When methanol is used as the participating solvent during ozonolysis of the PAHs significant variations on the standard procedure were observed. Pyrene **1** and B[e]P **4** reacted at the same position as without a participating solvent, however, the ozonides **1a** and **4a** were obtained in smaller amounts and were no longer the major product. Instead the methoxy ester **1c** and **4c** from the acid degraded peroxide (degrading in the HPLC by TFA buffer) were identified as the major products. For perylene **2**, again the aldehyde **2b**, saturated aldehyde **2a**, carboxylic acid **2c** were obtained, and also the acid-degenerated methanol trapped carbonyl oxide **2d** is obtained in small amounts. The black precipitate from perylene **2** still formed. For triphenylene **5**, still no major products were isolated. For acenaphthylene **6**,

the methoxy peroxide **6c** was detected and now also the ozonide **6a** was obtained and only traces of white polymer precipitate were observed. The mono-ozonide **6a** was isolated as a white solid using prep HPLC in 11% yield (qNMR conversion was 17% to **6a**). The peroxide **6c** was detected in the crude ¹H NMR spectrum, attempting to isolate it by preparative HPLC was not successful. Since this compound is known and its ¹H NMR shifts,²⁷ qNMR of the crude spectrum could still be done and a conversion of 40% to the methanol trapped peroxide **6c** was obtained. Sugimoto *et al.*,²⁷ reported yields of 13% of **6a** and 66% of **6c** at 0 °C, and 7% **6a** and 69% **6c** at –70 °C when performing the ozonolysis of **6** in DCM : MeOH. Ozonolysis of **1** in DCM : MeOH, was also reported in that study, and at 0 °C with a 66% conversion of **1**, they isolated ozonide **1a** in 9% and **1c** in 35%. Anthracene **7** reacted the same way as for under dry conditions.

Table 3 describes the conditions and results of the ozonolysis of selected PAHs for which products were isolated and characterized when methanol was used a participating solvent.

From these results, it can be proposed that when treating defect free graphene and GNRs with ozone and methanol, there will be ozonides, aldehydes, methoxy esters and carboxylic acids on the armchair edges and corners and carbonyls that might tautomerize to phenols on the zigzag edges.

Edge structure–reactivity correlation of ozonolysis of PAHs

In summary, ozone reacts *k* regions (part of armchair edges) and alkene ‘defect’ motifs, resulting in ozonides, aldehydes, esters and carboxylic acids depending on reaction conditions (*e.g.* solvents) when ozone reacts with zigzag motifs, ketones form regardless of conditions.

Zigzag edges has been reported to be more reactive towards oxidation than armchair edges.¹ The acenes, a group of PAHs which are all linear and contain zigzag edges, have been reported to be very reactive towards ozone. Ozone can undergo electrophilic aromatic substitution (EAS) with zigzag edges and

Table 3 Ozonolysis of compound **1–2**, **4–6** in DCM : MeOH (1 : 1, 0.025 mmol scale) or DCM-d₂ : MeOD (1 : 1, 0.01 mmol scale) at 20 °C. All conversions are from quantitative ¹H NMR spectroscopy with 1,2-DCE as internal standard and the error is 1%

Scale, mmol	V, mL	Ozone time, s	Substrate (conversion of %)	Product (conversion to %)
0.01	2	5	1 (38)	1a (9), 1c (22), 1e (0)
0.025	4	25	1 (78)	1a (18), 1c (29), 1e (0)
0.01/2 ^a	2/2	+5	1 (88)	1a (19), 1c (30), 1e (10)
0.025	4	25	2 (92)	2a (8), 2b (3), 2c (12), 2d (4)
0.01	2	5	4 (38)	4a (4), 4b (0), 4c (11), 4d (0)
0.025	4	25	4 (78)	4a (16), 4b (0), 4c (37), 4d (6)
0.01/2 ^a	2/2	+5	4 (92)	4a (12), 4b (10), 4c (36), 4d (0)
0.01	2	15	6 (100)	6a (8), 6c (20)
0.025	4	50	5 (24)	No detectable ^b product
0.01/2 ^a	2/2	+15	5 (48)	No detectable ^b product
0.01	2	5	7 (85)	7a (17)
0.01	2	+5	7 (86)	7a (17)

^a The 0.01 mmol scale experiments were performed by dissolving 0.01 mmol PAH in 2 mL DCM-d₂, followed by ozone treatment and leaving the sample for 30 min at 20 °C, then half the sample was transferred to a NMR tube and 1,2-DCE was added and half was treated with as much ozone again before it too was transferred to a NMR tube and 1,2-DCE added. ^b No new peaks in the ¹H NMR spectrum.



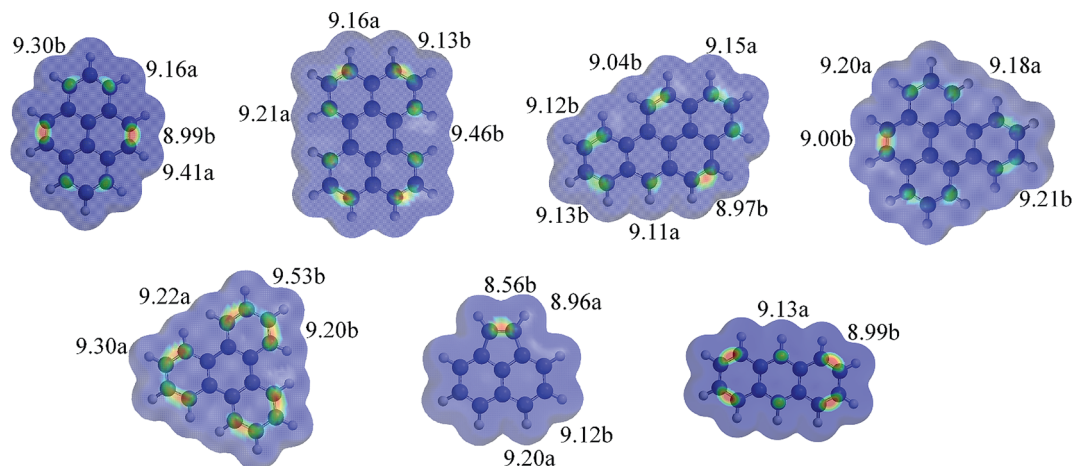


Fig. 1 PAHs 1–6 calculate local ionization energy (IE, in eV) surfaces. The values for the two–three lowest IE values for bonds (b) and atoms (a) are shown. The brighter areas between two atoms are predicted to be more reactive toward oxidative addition. Property range: 9.0–9.4 eV. See ESI† for all values.

both B[a]P 3 and anthracene 7 have been reported to yield the quinones upon ozonolysis.^{15,17,24,34}

Here, both B[a]P 3 and anthracene 7 was observed to be very reactive towards ozone and from PAH 7, anthraquinone 7a was observed. Pyrene 1 and B[e]P 4 (k region) have a similar reactivity towards ozone, triphenylene 5 (bay region) is less ozone reactive, and anthracene 7 (zigzag) is more reactive than 1 and 4. This corresponds nicely with the study by Pryor *et al.*¹⁶ where the relative ozone reactivity of PAHs, including 1, 2, 5 and 7 in dichloromethane was investigated. The least reactive was PAH 5, followed by 1, 2, then 7 being the most reactive PAH.

For hydrogen-terminated graphene, ozonation could possible lead to chemical differentiation of the edges which could be used for covalent stitching of graphene sheets and a study³⁵ recently showed that the electron mobility of the connection depends on how the edges of two graphene sheets are connected (*e.g.* zigzag–zigzag or armchair–armchair *etc.*) as well as the entity connecting the sheets.

Calculated local ionization energy surfaces

Both regiochemical and functional group outcome from the ozone treatment will depend on if the ozone attaches to the C=C bond (addition) or at a C atom (initial EAS) and ozone can react with sp^2 carbon motifs by both,^{10,34} although the preferred route for alkenes is cycloaddition of the electrophilic ozone 1,3-dipole.³⁶

Predicting reactivity for PAHs and possible also for larger systems (*e.g.* graphene and GNRs) are of importance for development of safe and selective processes. Local ionization energy surfaces (IES) is one computational tool, by which the most nucleophile sites in PAHs can be predicted. Depending on the localization of the minimum, the likely reaction outcome will either be electrophilic aromatic substitution (if the minimum is localized over an atom) or electrophilic addition (if the minimum is localized between two atoms).³⁷

Calculations of local IES for PAHs 1–7 was performed as described by Brown and Cockcroft³⁷ and the results compared to the experimental findings (previous sections). Generally, the calculated local IES correlates well to the experimental results. The major products from PAH 1, 4 and 6's were easily obtained under the right conditions; all have one double bond that is clearly more reactive than the others. The major product from perylene 2 was a polymer, possibly this formed from the initial product from ozone either adding to the bond with the lowest IE value or substituted to the atom with the lowest IE value. B[a]P 3, where many different products were observed, have four different bonds with similar IE values, and a zigzag edge. This correlates well with the observation of many different products forming already at short reaction times. Triphenylene 5 has six equal bonds with the same IE values and the observation of no major product, only slow degradation to many minor products is also in accordance with these calculations. Lastly, from anthracene 7 the quinone 7a was the only identified product, although the conversion of 7 was high.

PAHs 1–7 local IES are shown in Fig. 1, and the numbers are the most reactive positions for EAS and oxidative addition.

Conclusions

Six previously unreported compounds have been isolated from the ozonation of pyrene 1, perylene 2, benzo[e]pyrene 4. Studying different PAHs reaction with ozone, calculated local IESs and the literature indicate that ozone reacts with zigzag regions forming ketones regardless of any co-reagents and with the *k* region of the armchair edge, resulting in ozonide-, aldehyde-, carboxylic acid- or ester-groups depending on co-reagents. Ozone has a preference for zigzag edges over armchair edges. In practice, since ozone reacts with both, the reaction time and relative abundance of the edge motif are key factors for achieving regioselectivity.

The calculated local IESs correlates well against the experimental results indicating that this computational tool can be



used for predicting regioselectivity of ozone addition to larger PAH systems *e.g.* hydrogen-terminated graphene and GNRs.

Experimental section

General

All reagents were commercially available and used without further purification. NMR spectra were recorded on a Varian UNITY (^1H at 399.97 MHz, ^{13}C at 100.58 MHz) or a Varian INOVA (^1H at 499.93 MHz, ^{13}C at 125.71 MHz) spectrometer. The chemical shifts are reported using the residual solvent signal as an indirect reference to TMS ^1H : CHCl_3 : 7.26, acetone- d_6 : 2.05, DCM-d_2 : 5.32, MeCN-d_3 : 1.94 ^{13}C : CDCl_3 : 77.0. The vials used in all experiments were heavy-walled glass Emrys process vials (2–5 mL) sealed with aluminium crimp caps fitted with a septum. Ozone generator (Pilodist OGF 505) settings for all experiments were 5W, 0.25 bar, 0.5 L min^{-1} . See ESI† for HPLC UV traces and NMR spectra.

Calibration of the quantitative ^1H NMR spectroscopy method

Mixed stock solutions in vials with screw cap. Stored all stock solutions in freezer until use. Stock solution A: weighted 20.0 mg pyrene into a 2 mL vial. Added 1000 μL DCM-d_2 to the vial, sonicated until all pyrene dissolved. Stock solution B: added 3×1000 μL MeCN-d_3 into a 4 mL vial (screw cap), added 10.0 μL 1,2-DCE. Stock solution C: added 4 mL MeCN-d_3 into a 4 mL vial.

Prepared samples. To five (1–5) 4 mL vials, 2500 μL stock solution C was added (500 μL per vial). Added 2500 μL of stock solution B to vials 1–5 (500 μL per vial). Treated vial 1–3 with ozone at 20 $^\circ\text{C}$ for 15 s per vial. Standing at 20 $^\circ\text{C}$ for 10 min with cap on. Added 500 μL of stock solution A to vial 1–5 (100 μL per vial). The five solutions were transferred to NMR tubes and analyzed by ^1H NMR spectroscopy with $d_1 = 30$ s.

Setting internal standard integral (4H) to 400 resulted in pyrene (4H) integral or pyrene (4H) + **1a** (4H) integral values of: 1: 158 (140 + 18), 2: 157 (140 + 17), 3: 154 (138 + 16), 4: 154, 5: 156 (std dev 1%).

Acceptable inaccuracies for precise, accurate quantification using qNMR are 2%.³⁸

Preparative HPLC

As solvents acetonitrile and water was used with 0.01% TFA.

For all mixtures the same conditions were used.

After crude ^1H NMR spectroscopy, the NMR solution was injected in the prep HPLC. Injected volume: 600 μL , collected volume: 5 mL, flow rate: 20 mL min^{-1} , gradient: 20 to 90 (MeCN) over 20 min, 15 min isocratic (90% MeCN), UV detector: 254 nm, column: C18-PFP, 25 mm, 150 mm, 5 μm , 100 \AA . Removed solvent from collected fractions *in vacuo*, redissolved in 0.5 mL acetone- d_6 .

Calculation of local ionization energy surfaces

The structures was optimized using B3LYP/6-311G(d) with Gaussian 09 rev C.01 and Spartan 10. Local ionization energy surfaces were calculated at the same level using Spartan 10.

General procedure “small scale” (0.01 mmol) for quantitative ^1H NMR spectroscopy

Stock solutions of PAHs **1**, **2**, **4** and **5** (0.1 mmol mL^{-1}) using DCM-d_2 as solvent were prepared and of internal standard 1,2-DCE (20 μL in 4000 μL) using MeCN-d_3 as solvent.

PAH stock solution (100.0 μL , 0.01 mmol), internal standard stock solution (100 μL , 0.006 mmol 1,2-DCE) and deuterated solvent (tot. 1800 μL of D_2O , MeOD, DCM-d_2 and/or MeCN-d_3) was added to the vial. The vial was sealed with a cap.

The cap was removed and the reaction mixture bubbled through with ozone (PAH **1**: 5 s, **4**: 5 s, **5**: 15 s) at 20 $^\circ\text{C}$. The mixture was left at 20 $^\circ\text{C}$ for 30 min and half the total volume was transferred to an NMR tube. The mixture in the vial was again bubbled through with ozone (**1**: 5 s, **4**: 5 s, **5**: 15 s) and left to stand at 20 $^\circ\text{C}$ for 30 min before being transferred to a NMR tube. Reference samples for the internal standard were done for all experiments, were O_2 was used instead of O_3 . All NMR samples were analyzed by ^1H NMR spectroscopy with a d_1 of 30 s.

General procedure “medium scale” (0.025 mmol) for quantitative ^1H NMR spectroscopy

To a vial, PAH (0.025 mmol) was added, the vial was sealed with a cap and solvents (tot 4 mL) was added *via* a syringe through the cap. The reaction mixture was bubbled through with ozone (PAH **1**: 25 s, **2**: 25 s, **4**: 25 s **5**: 50 s) at 20 $^\circ\text{C}$. The mixture was left at 20 $^\circ\text{C}$ for 30 min and the solvent was removed *in vacuo* and any isolated solid or liquid was re-dissolved in acetone- d_6 (1 mL) and 1,2-DCE as internal standard and analyzed by ^1H NMR spectroscopy with $d_1 = 30$ s.

General procedure “large scale” (0.1 mmol) for isolation of products

To a vial, PAH (0.1 mmol) was added, the vial was sealed with a cap and solvents (total volume: 20 mL) was added *via* a syringe through the cap. The reaction mixture was bubbled through with ozone (**1**: 90 s, **2**: 90 s, **3**: 70 s, **4**: 90 s **5**: 300 s). The mixture was left at 20 $^\circ\text{C}$ for 1–2 hours and left in the freezer (-18 $^\circ\text{C}$) if left over night or longer. The solvent was removed *in vacuo* and all isolated solid or liquid was re-dissolved in acetone- d_6 (1.0 mL) and analyzed by ^1H NMR spectroscopy.

The solution was purified by preparative HPLC.

Additional procedures for the different conditions

Dry conditions. Dry DMC, vials dried in oven over night. SM added upon taking them out of oven and capped, cooled down under Ar(g) .

Water as a co-solvent. $\text{DCM} : \text{MeCN} : \text{H}_2\text{O}$ (8 : 11 : 1).

Methanol as a co-solvent. $\text{DCM} : \text{MeOH}$ (1 : 1).

Characterization data for isolated compounds

From pyrene **1**

Monoazonide 1a. ^1H NMR (500 MHz, acetone- d_6) δ 8.15 (d, $J = 7.2$ Hz, 2H), 7.98 (s, 2H), 7.85 (d, $J = 7.2$ Hz, 2H), 7.73 (dd, $J = 7.2$ Hz, 2H), 6.89 (s, 1H) ppm.



^{13}C NMR from HMBC (126 MHz, acetone) δ 106.8, 128.5, 128.8, 130.8, 132.8, 135.6, 135.9, 136.4 ppm.

Shifts and assignments in accordance with literature.³⁹

m/z [APCI⁺]: 251 (M⁺), 235, 236, 237, 205, 206, 207.

Hydroxy ester 1b. ^1H NMR (500 MHz, acetone- d_6) δ 8.32 (d, $J = 7.7$ Hz, 2H), 8.14 (d, $J = 7.7$ Hz, 2H), 7.97 (s, 2H), 7.86 (dd, $J = 7.7$ Hz, 2H), 7.41 (s, 1H), 6.79 (s, 1H) ppm.

^{13}C NMR from HMBC (126 MHz, acetone) δ 95.8, 124.1, 124.3, 127.2, 127.5, 127.7, 129.7, 130.6, 132.2, 133.2, 133.5, 133.6, 134.6, 134.8, 137.0, 168.4.

Shifts and assignments in accordance with literature (except the 7.41 PhCHOH shift in the ^1H NMR spectrum which was reported at 3.35 and mixed up with the PhCHOH shift at 6.79).⁴⁰

m/z [APCI⁺]: 251 (M⁺), 252, 253.

Methoxy ester 1c. ^1H NMR (500 MHz, acetone- d_6) δ 8.39–8.31 (m, 2H), 8.17 (dd, $J = 7.9$, 1.4 Hz, 1H), 8.02 (d, $J = 7.9$ Hz, 1H), 7.99 (ds, 2H), 7.87 (dd + dd, $J = 22.3$, 7.8 Hz, 2H), 6.40 (s, 1H), 3.79 (s, 3H) ppm.

Shifts and assignments in accordance with literature.⁴¹

m/z [APCI⁺]: 265 (M⁺), 266, 267.

Trialdehydecaboxylic acid 1d. ^1H NMR (500 MHz, acetone- d_6) δ 9.74 (s, 2H), 9.68 (s, 1H), 8.41 (d, $J = 9.2$ Hz, 1H), 8.26 (d, $J = 7.7$ Hz, 2H), 7.94–7.82 (m, 2H) ppm.

m/z [APCI⁺]: 283 (M⁺), 282, 267, 265.

HRMS [TOF MS ES⁺]: C₁₆H₁₀O₅, calculated: 283.0606, found: 283.0597.

Tetraaldehyde 1e. ^1H NMR (500 MHz, acetone- d_6) δ 9.78 (s, 4H), 8.35 (d, $J = 7.7$ Hz, 4H), 7.98 (dd, $J = 7.7$ Hz, 2H) ppm.

Shifts and assignments in accordance with literature.³¹

m/z [APCI⁺]: 267 (M⁺), 269.

From perylene 2

Unsaturated aldehyde cis-2a. ^1H NMR (500 MHz, acetone- d_6) δ 9.92 (d, $J = 7.8$ Hz, 1H), 8.86 (d, $J = 15.8$ Hz, 1H), 8.81 (d, $J = 7.3$ Hz, 1H), 8.79 (d, $J = 7.8$ Hz, 1H), 8.69 (dd, $J = 7.3$, 1.3 Hz, 1H), 8.26 (d, $J = 7.6$, 1H), 7.93 (td, $J = 7.6$, 4.2 Hz, 2H), 7.85 (dd, 1H), 7.77 (d, $J = 7.5$ Hz, 1H), 6.54 (dd, $J = 15.8$, 7.8 Hz, 1H) ppm.

^{13}C NMR from HMBC (126 MHz, acetone) δ 194.2, 185.5, 155.2, 139.2, 138.5, 138.3, 136.0, 132.9, 131.5, 130.8, 130.3, 129.5, 129.3, 129.2, 128.1, 128.0, 127.5, 127.0, 126.6, 124.9 ppm.

m/z [APCI⁺]: 285 (M⁺), 286, 287.

HRMS [TOF MS ES⁺]: C₂₀H₁₂O₂, calculated: 285.0916, found: 285.0910.

Aldehyde 2b. ^1H NMR (500 MHz, acetone- d_6) δ 10.74 (s, 1H), 8.85 (dd, $J = 11.9$, 8.2 Hz, 2H), 8.72 (dd, $J = 7.3$, 1.2 Hz, 1H), 8.51 (dd, $J = 8.2$, 1.2 Hz, 1H), 8.28 (d, $J = 8.2$ Hz, 1H), 7.97 (dt, $J = 14.0$, 7.6 Hz, 2H), 7.87 (dd, $J = 7.9$, 1H), 7.70 (dd, $J = 7.7$, 1.1 Hz, 1H) ppm.

m/z [APCI⁺]: 259 (M⁺), 260.

Carboxylic acid 2c. ^1H NMR (500 MHz, acetone- d_6) δ 8.80 (d, $J = 7.1$ Hz, 1H), 8.72 (dd, $J = 8.2$, 1.0 Hz, 1H), 8.66 (dd, $J = 7.3$, 1.3 Hz, 1H), 8.46 (d, $J = 9.1$ Hz, 1H), 8.25 (d, $J = 8.1$ Hz, 1H), 7.91 (ddd, $J = 8.2$, 7.4, 2.1 Hz, 2H), 7.85 (dd, $J = 7.4$, 1H), 7.58 (dd, $J = 7.4$, 1.0 Hz, 1H) ppm.

m/z [APCI⁺]: 275 (M⁺), 276, 277.

HRMS [TOF MS ES⁻]: C₁₈H₁₀O₃, calculated: 273.0552 (M – H⁻) found: 273.0553 (M – H⁻).

Methyl ester 2d. ^1H NMR (500 MHz, acetone- d_6) δ 8.83 (d, $J = 7.4$ Hz, 1H), 8.77 (d, $J = 8.1$ Hz, 1H), 8.69 (dd, $J = 7.4$, 1.4 Hz, 1H), 8.50 (dd, $J = 8.1$, 1.4 Hz, 1H), 8.29 (d, $J = 8.1$ Hz, 1H), 7.95 (dd, $J = 8.1$ Hz, 2H), 7.88 (dd, 1H), 7.58 (dd, $J = 7.4$, 1.1 Hz, 1H), 3.98 (s, 3H) ppm.

^{13}C NMR from HMBC (126 MHz, acetone) δ 177.2, 165.5, 131.9, 131.1, 130.8, 130.7, 128.3, 126.2, 125.5, 124.7, 123.1, 123.0, 122.6, 122.6, 122.5, 121.4, 120.4, 119.9, 47.0, ppm.

m/z [APCI⁺]: 289 (M⁺), 290, 291.

HRMS [TOF MS ES⁺]: C₁₉H₁₂O₃, calculated: 289.0865 found: 289.0871.

From benzo[e]pyrene 4

Benzo[e]pyrene monoazonide 4a. ^1H NMR (500 MHz, acetone- d_6) δ 9.04 (dd, $J = 8.2$, 1.5 Hz, 2H), 8.82 (dd, $J = 6.3$, 3.3 Hz, 2H), 7.86 (dd, $J = 8.2$, 1.5 Hz, 2H), 7.79 (dd, $J = 8.2$, 7.2 Hz, 1H), 7.75 (dd, $J = 6.3$, 3.3 Hz, 1H), 6.87 (s, 1H) ppm.

^{13}C NMR from HMBC (126 MHz, acetone) δ 130.6, 127.0, 122.9, 122.2, 120.7, 130.6, 118.8, 124.6, 122.1, 100.4.

HRMS [TOF MS ES⁺]: C₂₀H₁₂O₃, calculated: 301.0865 found: 301.0866.

Benzo[e]pyrene dialdehyde **4b** and benzo[e]pyrene acid-degenerated water trapped carbonyl oxide **4c** only as ^1H NMR spectra on crude products. Shifts used for qNMR spectroscopy; **4b**: 8.79, 8.68, 8.03, 6.16, **4c**: 8.74, 7.92 6.20, 5.60, 3.79.

From acenaphthylene 6

Acenaphthylene monoazonide 6a. Isolated as a white solid (4.5 mg, 11%) by preparative HPLC by following the general procedure for larger scale, performing this in duplicates and pooling the crudes prior to purification.

^1H NMR (500 MHz, acetone- d_6) δ 8.00 (dd, $J = 8.2$, 1.2 Hz, 2H), 7.64 (dd, $J = 6.9$, 1.2 Hz, 2H), 7.59 (dd, $J = 8.2$, 6.9 Hz, 2H), 6.96 (s, 2H) ppm.

Shifts and assignments in accordance with literature.²⁷

Acenaphthylene methoxyperoxide 6c. Not isolated. Used the NMR literature values for the integration of the qNMR spectrum of the crude product. ^1H NMR: δ 3.69 (s, 3H), 6.09 (s, 1H), 6.49 (s, 1H), 7.2–7.9 (m, 6H), 9.45 (s, 1H) ppm.²⁷

From anthracene 7

Anthraquinone 7a. Not isolated. Used the NMR values from a bought sample of **7a** for the integration of the qNMR spectrum of the crude product. ^1H NMR: δ 7.81 (m, 4H), 8.32 (m, 4H) ppm.

Conflict of interest

The authors declare no competing financial interests.

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