Final Technical Report

Abstract

Project Title: High Temperature Chemistry of Aromatic Hydrocarbons

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Year Started: 1993

Overall Research Goals

The primary goal of this research was to uncover the principal reaction channels available to polycyclic aromatic hydrocarbons (PAHs) at high temperatures in the gas phase and to establish the factors that determine which channels will be followed in varying circumstances. New structure-property relationships for PAHs were also studied.

DOE Interest

The efficient production of clean energy from fossil fuels will remain a major component of the DOE mission until alternative sources of energy eventually displace coal and petroleum. Hydrocarbons constitute the most basic class of compounds in all of organic chemistry, and as the dominant species in fossil fuels, they figure prominently into the programs of the DOE. Much is already known about the normal chemistry of hydrocarbons under ambient conditions, but far less is known about their intrinsic chemistry at temperatures close to those reached during combustion. An understanding of the fundamental molecular transformations, rearrangements, and interconversions of PAHs at high temperatures in the gas phase, as revealed by careful studies on small, well-designed, molecular systems, provides insights into the underlying chemistry of many important processes that are more complex, such as the generation of energy by the combustion of fossil fuels, the uncatalyzed gasification and liquefaction of coal, the production of fullerenes in fuel-rich flames, and the formation of soot and carcinogenic pollutants in smoke (*e.g.*, benzo[*a*]pyrene). The rational control of any of these processes, whether it be the optimization of a desirable process or the minimization of an undesirable one, requires a clear knowledge of the basic chemistry that governs the fate of the species involved.

Advances in chemistry at the most fundamental level come about primarily from the discovery of new reactions and from new insights into how reactions occur. Harnessing that knowledge is the key to new technologies. The recent commercialization of a combustion synthesis of C_{60} and other fullerenes depended critically on a knowledge of hydrocarbon reactions at high temperatures in the gas phase, and the research supported by this project enabled further advances in the realm of carbon-rich materials.

Significant Achievements and Results Since July 1, 2012

The picture for how aryl–aryl bonds cleave at high temperatures in the gas phase is now clearer.

- We obtained the first evidence that substituted phenyl radicals really can “explode,” leaving ethynyl or butadiynyl fragments attached to the arene.

- We also determined that the “explosion” of phenyl radicals, although real, does not contribute in a major way to the mechanism of aryl–aryl bond cleavage at 1100 °C in the gas phase.

- Evidence was found *against* the mechanism for aryl–aryl bond cleavage that begins with attachment of a hydrogen atom *ipso* to the phenyl group that is lost.

- The first evidence *against* the benzyne-loss mechanism was also obtained.

- New experimental evidence was acquired that argues *against* direct homolysis of $C(sp^2)–C(sp^2)$ bonds as the primary reaction pathway for aryl-aryl bond cleavage reactions at high temperatures in the gas phase.

- We obtained the first evidence *against* the hydrogen-shift/carbene insertion mechanism for thermal cyclodehydrogenations leading to new 5-membered rings.

- To test our hypothesis for the mechanism of acene-to-phenacene rearrangements of acene radicals, we synthesized 9-bromo-9-[^{13}C]anthracene and studied its behavior at high temperatures in the gas phase by flash vacuum pyrolysis (FVP). It behaves exactly as predicted by our proposed mechanism and provides strong evidence for the rupture of transannular bonds in *cata*-condensed aromatic hydrocarbon radicals.

- To determine the generality of acene-to-phenacene rearrangements of acene radicals, we synthesized 1-bromo-1-[^{13}C]naphthalene and studied its behavior under FVP conditions. As expected, rupture of the transannular bond in the 1-naphthyl radical is more difficult than rupture of the transannular bond in larger acene radicals. No ^{13}C-scrambling was detected that could be attributed to transannular bond rupture.

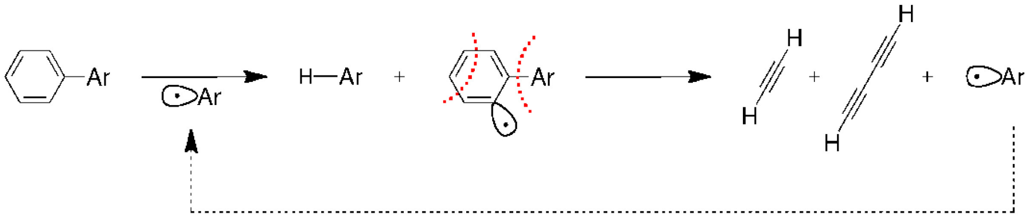
- We also synthesized 7-bromo-7-[^{13}C]benz[*a*]anthracene and studied its behavior under FVP conditions. Analysis of the products formed provided strong evidence for the rupture of the transannular bonds in the benz[*a*]anthracen-7-yl radical, as anticipated.

Research Findings Since July 1, 2012

1. "Explosion" of Phenyl Radicals

To the best of our knowledge, no counterpart for the uncatalyzed cleavage of aryl-aryl bonds has ever been observed under ordinary laboratory conditions. Considering the centrality of aryl-aryl bond cleavages in the gasification and liquefaction of coal, we have been seeking a more detailed mechanistic understanding of this fundamental process as a major component of our ongoing research. Scheme 1 shows how a phenyl group attached to a polycyclic aromatic hydrocarbon (PAH) might simply "explode" after losing a hydrogen atom under high energy conditions, thereby forming a "phenyl-loss product" (*i.e.*, Ph–Ar → H–Ar).

Scheme 1

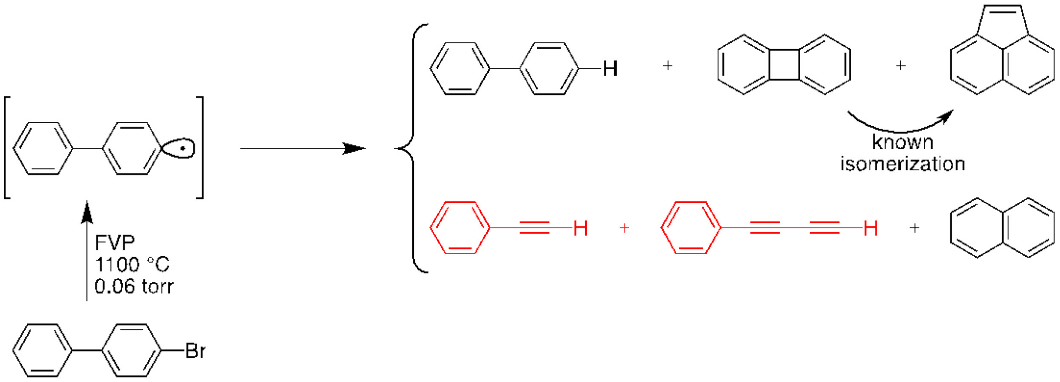


The initial loss of a hydrogen atom could occur either by direct homolysis of the C–H bond or by hydrogen atom-transfer to another radical. The PAH radical resulting from the "explosion" could then abstract a hydrogen atom from another molecule to give the phenyl-loss product (H–Ar) and initiate the process again. In this scenario, the original site of hydrogen atom loss is not critical, because aryl radicals are known (from our previous work) to interconvert by 1,2-shifts of hydrogen atoms at high temperatures in the gas phase.

Depending on the location of the radical center and which bonds break in the "explosion" of a substituted phenyl radical, fragments of the original phenyl group could remain attached to the PAH moiety. In the simplest case, biphenyl, the "explosion" of one phenyl group could lead to benzene or to phenylacetylene or to phenylbutadiyne, plus acetylene and/or 1,3-butadiyne. We have searched for this process and have now found evidence that substituted phenyl radicals really can "explode."

With our flash vacuum pyrolysis (FVP) apparatus, it is difficult to capture and identify small, volatile products such as acetylene (C_2H_2), butadiyne (C_4H_2), and even benzene (C_6H_6), but larger hydrocarbons, such as phenylacetylene (C_8H_6) and phenylbutadiyne ($C_{10}H_6$), are easy to detect by GC-MS. When 4-bromobiphenyl was subjected to FVP at 1100 °C/0.6 torr, homolysis of the Ar–Br bond generated the biphenylyl radical (initially in the 4-position), which lead to the formation of several products that were trapped at liquid nitrogen temperatures. Analysis of the product mixture revealed the presence of both phenylacetylene and phenylbutadiyne (Scheme 2). FVP of 2-bromobiphenyl gave comparable amounts of phenylbutadiyne and lesser amounts of phenylacetylene.

Scheme 2

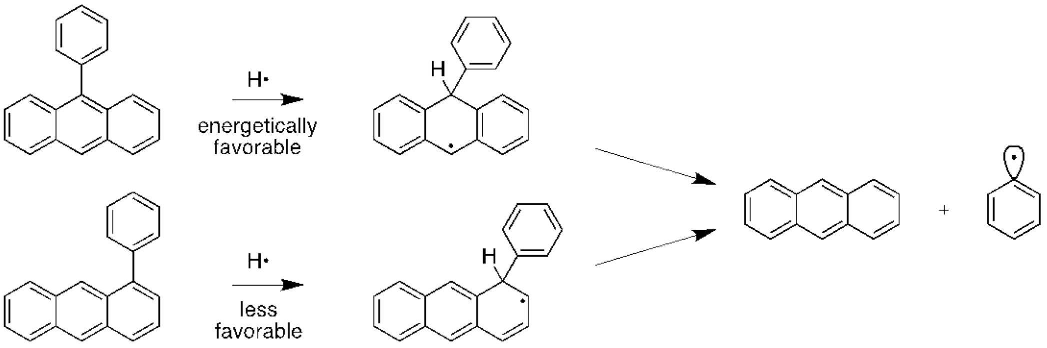


The formation of these 8-carbon and 10-carbon products provides undeniable evidence that one of the phenyl groups must have "exploded," blowing out a 4-carbon or 2-carbon fragment (presumably butadiyne or acetylene). Naphthalene, another 10-carbon product, must also be derived from loss of a 2-carbon fragment. The fact that these diagnostic compounds collectively constitute less than 1% of the total product mixture, however, reveals that "explosion" of the benzene ring is not a particularly significant reaction channel followed by substituted phenyl radicals at 1100 °C. Most of the biphenylyl radicals that give products larger than benzene either scavenge a hydrogen atom to make biphenyl or cyclize to make biphenylene, some of which then further isomerizes to acenaphthylene by a known pathway (Scheme 2).

2. Evidence Against *ipso* Attachment of a Hydrogen Atom as the Major Pathway for Aryl–Aryl Bond Cleavage

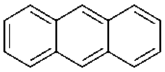
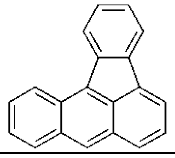
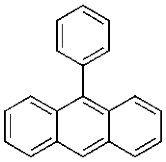
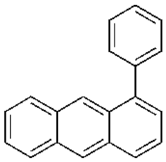
Another plausible mechanism for the cleavage of aryl-aryl bonds involves initial attachment of a hydrogen atom to the carbon atom of the arene that bears the other aryl group (*i.e.*, the *ipso* carbon). This pathway looks especially favorable for phenyl group loss from 9-phenylanthracene, because the proposed radical intermediate would be highly stabilized by two-fold benzylic resonance (Scheme 3). By comparison, 1-phenylanthracene is also capable of losing a phenyl group, but the hydrogen atom *ipso* attachment pathway should be significantly less favorable (Scheme 3). Calculations at the UB3LYP/6-31G* level of theory predict that *ipso* attachment of a hydrogen atom should be more favorable on 9-phenylanthracene than on 1-phenylanthracene by 8.2 kcal/mol.

Scheme 3



To probe this mechanistic proposal experimentally, we have now studied the FVP of both 1-phenylanthracene and 9-phenylanthracene under identical conditions and have determined the relative ease with which each loses a phenyl group. Table 1 summarizes our results.

Table 1. Products formed (relative %) from FVP at 1100 °C/0.6 torr.

starting material	recovered starting material		
	68.5	8.9	22.7[a]
	83.3[b]	4.7	12.0

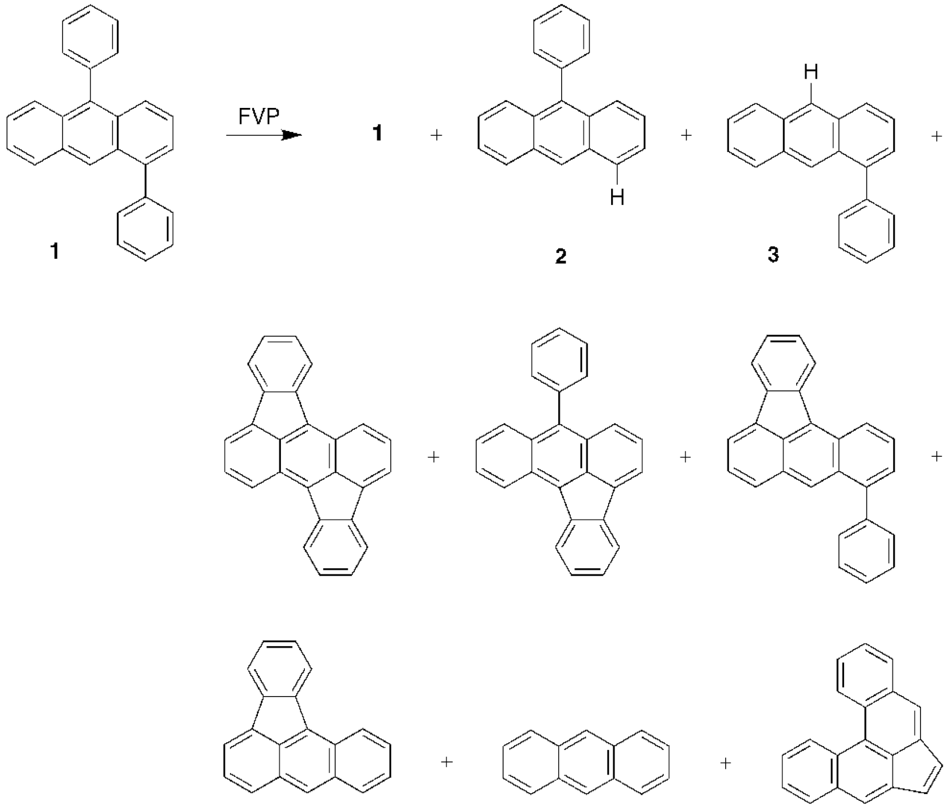
[a] Includes 5.7% that suffered subsequent isomerization to dibenzo[*e,h*]acenaphthylene. [b] Includes 3.9% that isomerized to 2-phenylanthracene.

Qualitatively, these results reveal that phenyl loss is indeed more favorable from 9-phenylanthracene than from 1-phenylanthracene, in agreement with the mechanism outlined in Scheme 3. The difference in reactivity, however, is less than 2-fold, which falls far short of the difference expected for the hydrogen atom *ipso* attachment pathway. Even at 1100 °C, a difference of 8.2 kcal/mol between the two reactions should lead to a reactivity difference of >10-fold.

The 2-fold difference in reactivity can be accounted for almost entirely by the steric crowding of the phenyl group in 9-phenylanthracene, which destabilizes this isomer relative to 1-phenylanthracene by 1.8 kcal/mol. These new results reinforce our conclusion based on earlier experiments that *ipso* attachment of a hydrogen atom is not a significant contributor to the mechanism of phenyl loss.

As a follow-up to this work, we have also conducted an internal competition experiment in which phenyl groups can be lost from either the central ring or the terminal ring of 1,10-diphenylanthracene (**1**). The mechanism for phenyl group loss that involves *ipso* attachment of a hydrogen atom would again be expected to strongly favor phenyl group loss from the central ring. Unlike the previous experiments, which relied on our ability to reproduce the FVP conditions precisely from one run to the next, this experiment guarantees that both phenyl–arene bonds are exposed to identical conditions (temperature, pressure, contact time, etc.) simultaneously. Experimentally, we see many products derived from cyclodehydrogenations and/or phenyl loss (Scheme 4). The most important observation, however, is that the relative ease of phenyl group loss to produce phenylanthracenes **2** and **3** again varies by less than a factor of 2. We cannot exclude the *ipso* attachment of hydrogen mechanism as a contributor the overall picture, but it certainly is **NOT** the only mechanism operating under our FVP conditions.

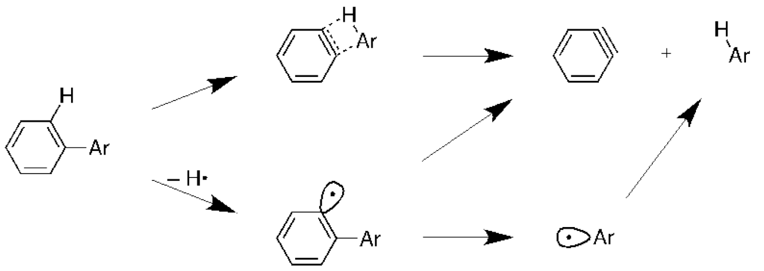
Scheme 4



3. Evidence Against Benzyne Loss as the Major Pathway for Aryl–Aryl Bond Cleavage

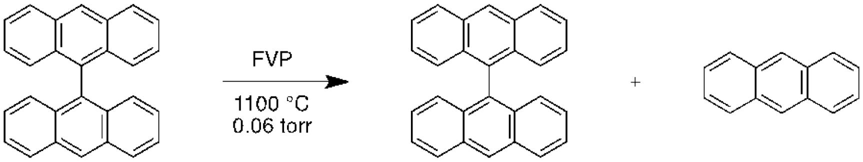
Scheme 5 shows how a phenyl group attached to a PAH might be lost as benzyne, either concertedly or after losing an *ortho* hydrogen atom under high energy conditions.

Scheme 5



Both of these pathways require the presence of an *ortho* hydrogen atom on the aryl group that is lost. To test whether or not aryl-aryl bond cleavages really do require the presence of an *ortho* hydrogen atom, we examined the high temperature chemistry of 9,9'-bianthracenyl, which has no hydrogen atoms *ortho* to the aryl-aryl bond. FVP of 9,9'-bianthracenyl at 1100 °C/0.6 torr was very clean and gave only recovered starting material and anthracene, the product of aryl-aryl bond cleavage (Scheme 6). In duplicate runs, the average extent of aryl-aryl bond cleavage was 11.0%. Comparing this result to the 8.9% of phenyl loss seen from 9-phenylanthracene under the same conditions (Table 1) leaves no doubt that an *ortho* hydrogen atom is NOT required for the cleavage of aryl-aryl bond at high temperatures in the gas phase under FVP conditions. We take this as compelling evidence *against* the benzyne-loss pathway for aryl-aryl bond cleavages.

Scheme 6



4. Evidence Against Aryl–Aryl Bond Cleavage be Direct C–C Bond Homolysis

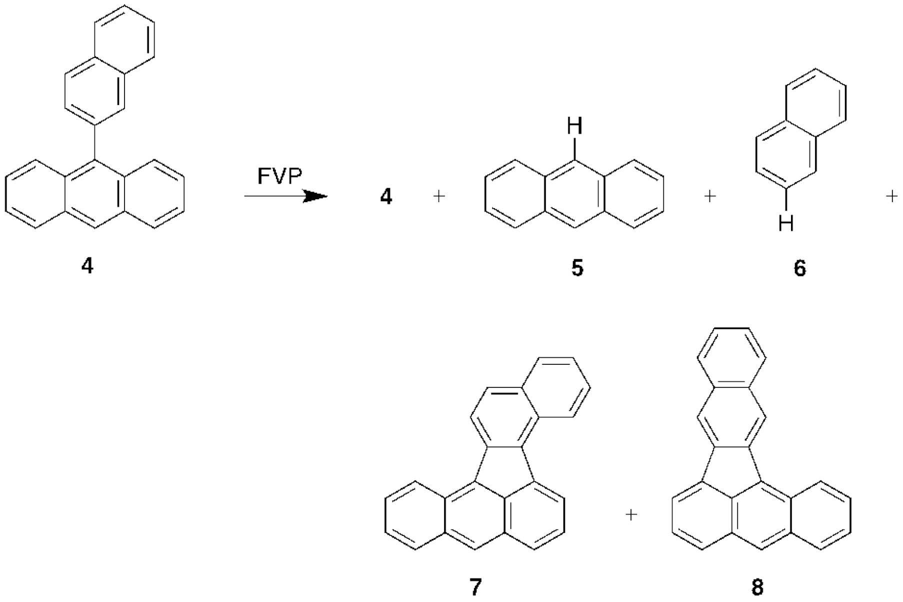
The most direct pathway to cleave an aryl-aryl bond is simple homolysis to generate two aryl radicals, which then scavenge hydrogen atoms with similar efficiency, giving the two constituent arenes as the observed products in comparable amounts (Scheme 7). The seemingly prohibitive enthalpic costs associated with this mechanism is actually offset to a great extent by the favorable entropic gain – *i.e.*, TΔS is quite large at 1100 °C at low pressures. Calculations at the UB3LYP/6-31G* level of theory predict a bond dissociation energy of 116.2 kcal/mol for the prototypical aryl-aryl bond in biphenyl, and that value matches closely the experimental number. Such calculations, however, consider only enthalpy at 0 K and ignore zero-point energy corrections, entropy contributions, and temperature effects on the enthalpy. Taking into account all of these corrections, homolysis of the aryl-aryl bond in biphenyl is calculated to drop to 97.4 kcal/mol at 25 °C and 1 atm pressure. Under the conditions of our FVP experiments (1100 °C/0.6 torr) all of these corrections make even larger contributions, and the entropic gain of forming two phenyl radicals from one biphenyl ($T\Delta S_{rxn} = -117.9$ kcal/mol) is enough by itself to pay the price for direct homolysis of the aryl-aryl bond in biphenyl.

Scheme 7

This prediction of a "negative bond energy" under extreme conditions almost certainly reflects some deficiencies in the mathematical model for computing entropy corrections, but it underscores how important entropy factors become at high temperatures and low pressures. Every other proposed mechanistic pathway for aryl-aryl bond cleavage that we have tested has failed to survive experimental scrutiny, and the accumulated evidence all points to simple homolysis to generate two aryl radicals, which then scavenge hydrogen atoms.

Because benzene is too volatile for us to trap and quantify reliably, we chose to study the FVP of an unsymmetrical biaryl in which both aryl groups are larger than a phenyl ring, so that we could see the products from both aryl groups. Toward this end, 9-(2-naphthyl)anthracene (**4**) was synthesized by Suzuki coupling of 9-bromoanthracene with naphthalene-2-boronic acid. Subsequent FVP of **4** gave mostly recovered starting material (*m/z* 304), plus a mixture of hexacyclic PAHs (*m/z* 302) that we tentatively assign to be the two isomeric products of thermal cyclodehydrogenation, dibenzo[*a,j*]fluoranthene (**7**) and dibenzo[*a,k*]fluoranthene (**8**), plus a significant amount of anthracene (**5**), one of the products of aryl–aryl bond cleavage. The other product of aryl–aryl bond cleavage, however, naphthalene (**6**), was found only in trace amounts (Scheme 8).

Scheme 8



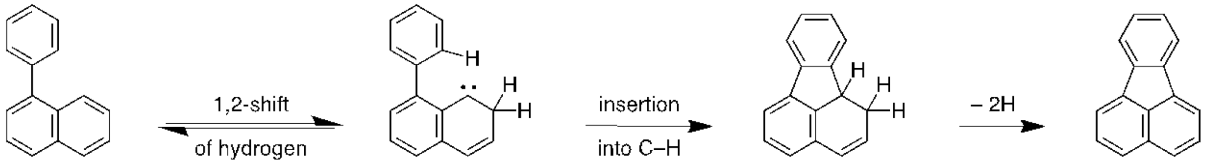
From the NMR spectrum of the crude product mixture, the ratio of recovered starting material (**4**) to anthracene (**5**) was determined to be 4.4:1, reflecting a substantial amount of aryl–aryl bond cleavage, but, surprisingly, no NMR signals could be seen for naphthalene (**6**). Analysis of the crude product mixture by GC-MS, which is more sensitive, revealed a tiny peak above the noise level for naphthalene (**6**); however, the ratio of anthracene (**5**) to naphthalene (**6**) in the product mixture from FVP of 9-(2-naphthyl)anthracene (**4**) was >10:1. Assuming that the two aryl radicals would scavenge hydrogen atoms to give the two constituent arenes with comparable efficiency, *the data from this experiment argue* ***against*** *the direct homolysis mechanism as a major contributor to the cleavage of aryl–aryl bonds under FVP conditions*.

All of these results, together with the results from earlier experiments in our lab, have now been published as a full paper in a special issue of the *Australian Journal of Chemistry* dedicated to the memory of the late R. F. C. Brown, one of the pioneers in pyrolysis chemistry. A contribution from our laboratory was invited by the editor.

5. Evidence Against the Hydrogen-Shift/Carbene Insertion Mechanism for Thermal Cyclodehydrogenations Leading to New 5-Membered Rings

For many years, we tried to gain insight into the mechanism by which aromatic hydrocarbons undergo thermal cyclodehydrogenations leading to new 5-membered rings. From our earlier work, we learned that the hydrogen atoms in PAHs can scramble by reversible 1,2-shifts that generate transient carbene intermediates. This suggested to us that the thermal cyclodehydrogenation of 1-phenylnaphthalene to fluoranthene (and similar cyclizations in larger systems) might follow the pathway depicted in Scheme 9.

Scheme 9



We now have evidence *against* this mechanism. In our recent studies on the FVP of 1- and 9-phenylanthracene, we saw not only phenyl loss but also thermal cyclodehydrogenations leading to new 5-membered rings (Table 1). The mechanism outlined in Scheme 9 would be available to 9-phenylanthracene, but the 1,2-shift of hydrogen in 1-phenylanthracene is blocked; shifting a hydrogen to an angular carbon atom would destroy the aromaticity of two benzene rings, rather than that of just one. If the hydrogen-shift/carbene insertion mechanism were to account for the thermal cyclodehydrogenations of 1- and 9-phenylanthracene, therefore, the former should be much more difficult than the latter.

Experimentally, we do observe a greater yield of thermal cyclodehydrogenation from 9-phenylanthracene than from 1-phenylanthracene (22.7% vs 12.0%, Table 1); however, the difference is less than 2-fold and can be accounted for almost entirely by the destabilization that 9-phenylanthracene suffers from steric crowding of the phenyl group (*vide supra*). The fact that the ratio of thermal cyclodehydrogenation to phenyl loss is exactly the same for both 9-phenylanthracene and 1-phenylanthracene (2.55 : 1) argues strongly for the absence of any special pathway available to one isomer but not the other for either reaction. We conclude that both are losing phenyl groups by the same mechanism, that both are cyclizing by the same mechanism, and that the mechanism for the latter is *not* a hydrogen-shift/carbene insertion pathway analogous to that in Scheme 9.

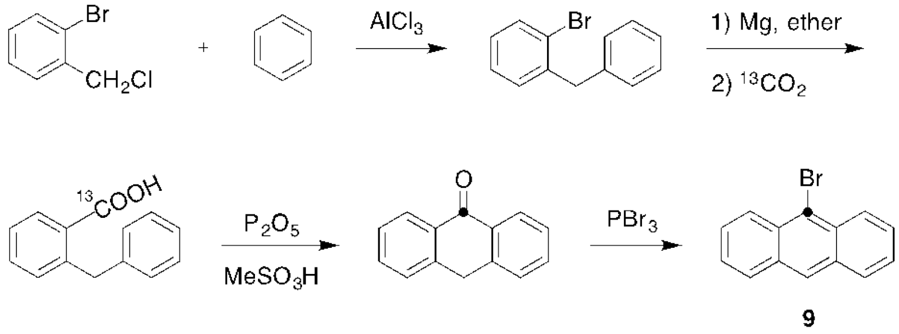
6. Evidence for the Rupture of Transannular Bonds in Acene Radicals

Some years ago, we discovered that FVP of 9-bromoanthracene yields primarily anthracene (the expected product from hydrogen scavenging) but that significant quantities of phenanthrene are also formed, along with several more highly unsaturated products in minor amounts. Under the same conditions, FVP of the parent hydrocarbon, anthracene, yields no more than trace quantities of phenanthrene. Clearly, the presence of a radical on the rim of anthracene opens up some mechanistic pathway that can isomerize the linear acene to the bent isomer, phenanthrene.

In our 2012 grant renewal application, we speculated that rupture of a transannular bond in the 9-anthracenyl radical could account for this unexpected skeletal isomerization and proposed a

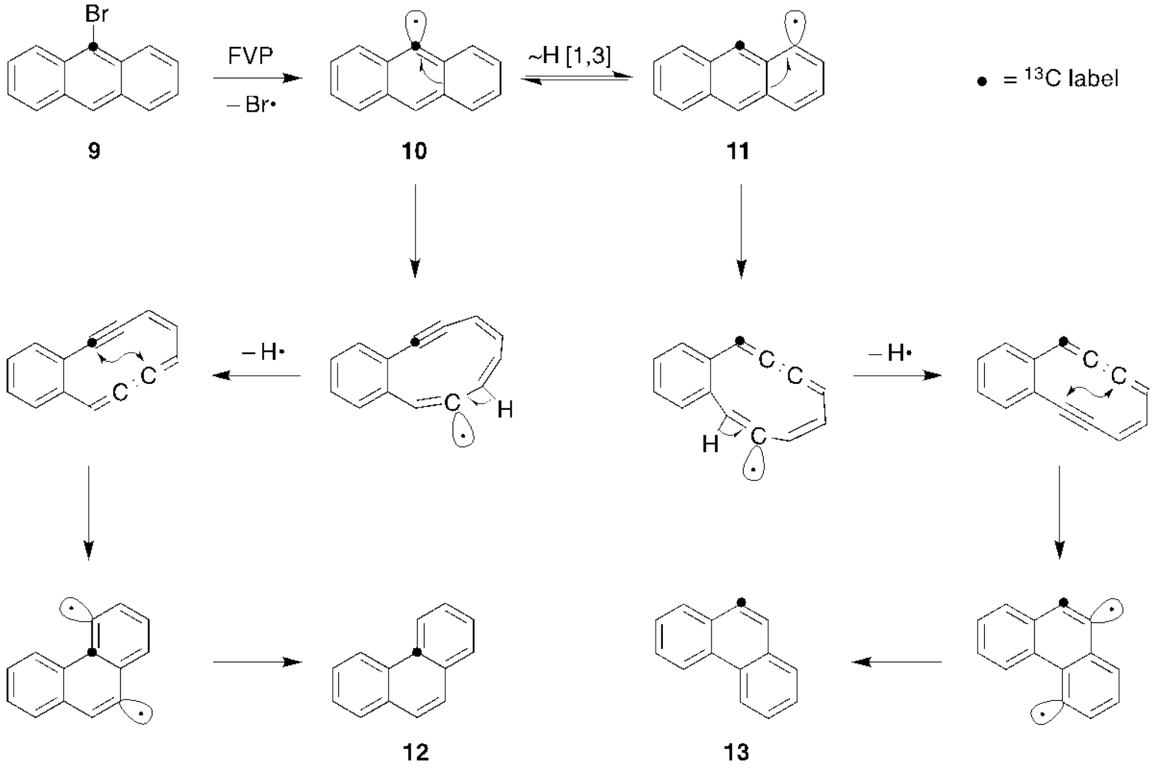
^{13}C-labeling study to test our hypothesis. We have now completed the synthesis of 9-bromo-9-[^{13}C]anthracene (**9**) as outlined in scheme 10 and have studied its FVP in detail.

Scheme 10



Scheme 11 shows that the mechanistic pathways we proposed predict the formation of two and only two isotopomers of ^{13}C-labeled phenanthrene: 4a-[^{13}C]phenanthrene (**12)** and 9-[^{13}C]phenanthrene (**13**). Experimentally, that is precisely what we see! The major product is 4a-[^{13}C]phenanthrene (**12**), and the only other significant product is 9-[^{13}C]phenanthrene (**13**). These two isotopomers are formed in a 60:40 ratio. The lesser amount of 9-[^{13}C]phenanthrene (**13**) reflects the slow but competitive intervention of a 1,3(*peri*)-hydrogen shift at the stage of the 9-anthracenyl radical (**10 <=> 11**). Earlier studies in our laboratory predicted and demonstrated experimentally the 1,3(*peri*)-hydrogen shift rearrangement in other aromatic hydrocarbons, so we were expecting it to show up here, too.

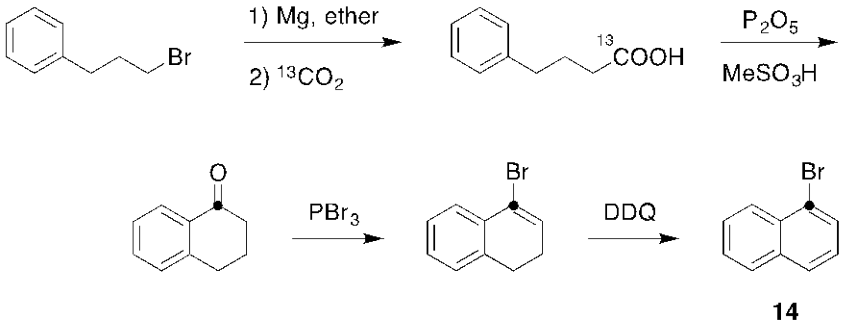
Scheme 11



7. Evidence *Against* the Rupture of Transannular Bonds in 1-Naphthyl Radicals

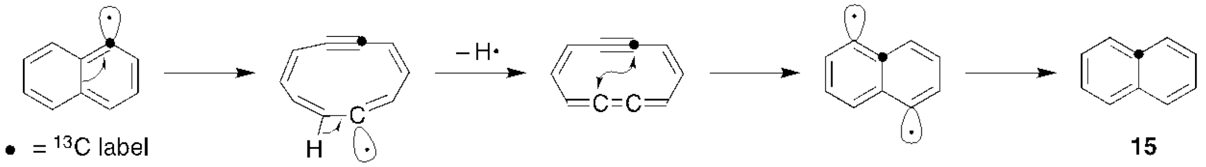
Calculations predict that rupture of the transannular bond in the 1-naphthyl radical should be more difficult than rupture of the transannular bond in the 9-anthracenyl radical (**10**). To look for the same isomerization in the naphthalene ring system, we synthesized 1-bromo-1-[^{13}C]naphthalene (**14**) as outlined in Scheme 12 and studied its flash vacuum pyrolysis (FVP) in detail.

Scheme 12



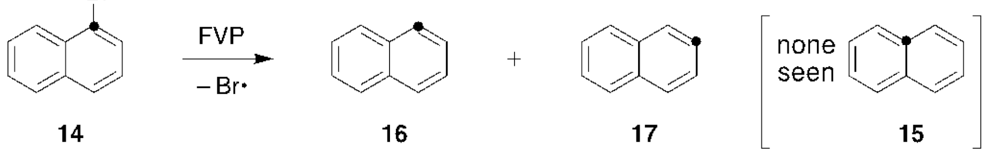
Rupture of the transannular bond in the 1-naphthyl radical is predicted to scramble the ^{13}C-label into the ring junction position of naphthalene (**15**, Scheme 13).

Scheme 13



Experimentally, FVP of 1-bromo-1-[^{13}C]naphthalene (**14**) at 1100 °C/0.5 mmHg gave 1-[^{13}C]naphthalene (**16**) and 2-[^{13}C]naphthalene (**17**) in a ratio of 8:3 (Scheme 14). Rupture of the transannular bond in the 1-naphthyl radical as shown in Scheme 13 would be expected to produce significant quantities of 4a-[^{13}C]naphthalene (**15**), but none was observed, within the limits of NMR detection (~5%).

Scheme 14



If the 1-[^{13}C]naphth-1-yl radical derived by homolysis of the C–Br bond in **14** fails to ring open as depicted in scheme 13, it should simply scavenge a hydrogen atom and give 1-[^{13}C]naphthalene (**16**). That appears to be the dominant process. The formation of

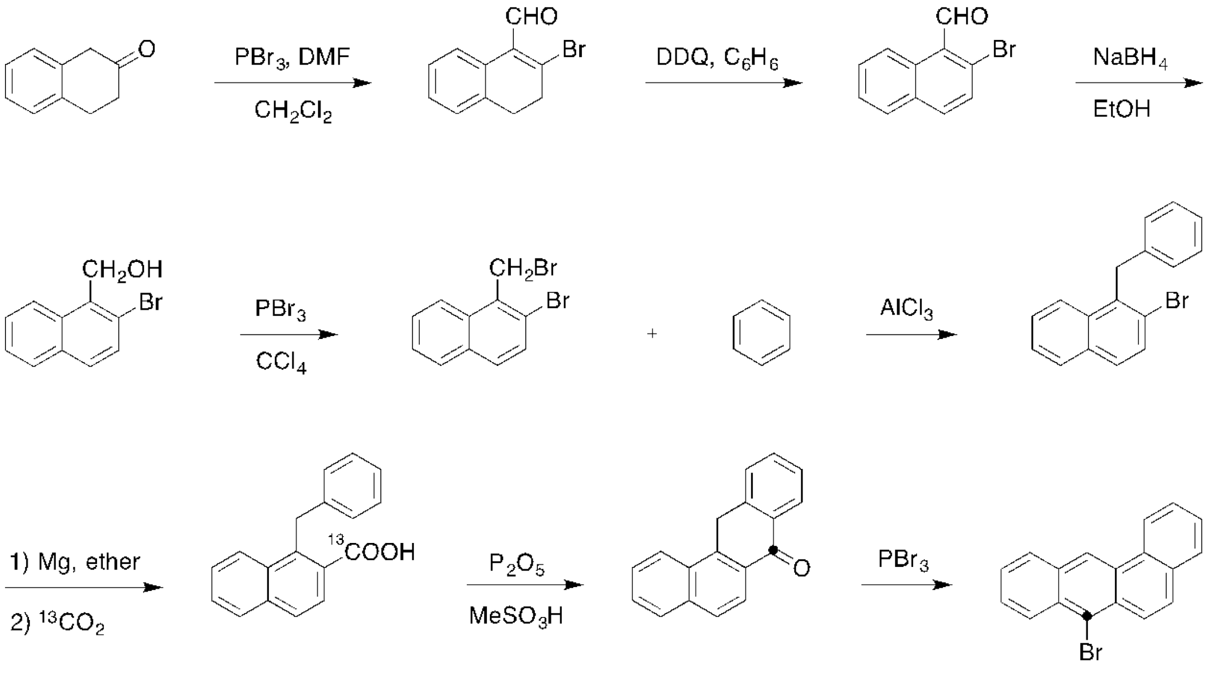
2-[^{13}C]naphthalene (**17**) most likely results from a secondary rearrangement of **16** to **17**, which is a known ^{13}C-scrambling reaction at 1100 °C.

We conclude from these experiments that rupture of the transannular bond in the 1-naphthyl radical is indeed more difficult than rupture of the transannular bond in the 9-anthracenyl radical and that it occurs only to a very minor extent at 1100 °C, if at all. These experiments provide further evidence that isomerization of the 9-anthracenyl radical to the phenanthrene ring system really does involve rupture of the transannular bond, as shown in Scheme 11.

8. Evidence for the Rupture of Transannular Bonds in the 7-benz[*a*]anthracenyl Radical

Transannular bonds in acene radicals larger than the 9-anthracenyl radical (**10**) are expected to rupture as easily as the transannular bonds in **10**, if not even more easily. To test this prediction, we synthesized 7-bromo-7-[^{13}C]benz[*a*]anthracene (**18**) as outlined in Scheme 15 and studied its behavior under FVP conditions.

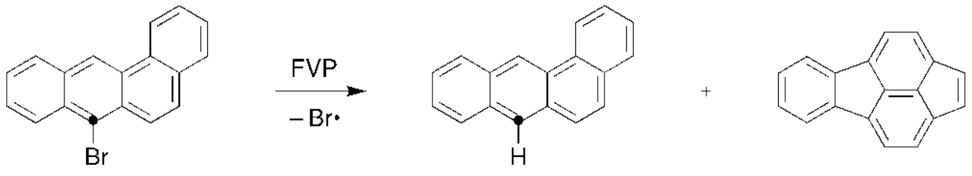
Scheme 15



18

FVP of **18** at 1000 °C and at 1100 °C/0.5 mmHg gives benz[*a*]anthracene (**19**), with all of the ^{13}C label still localized in position 7, and acefluoranthrylene (**20**), with the ^{13}C label distributed over several positions (Scheme 16). Hydrocarbon **20** is not the phenacene expected from the 7-[^{13}C]benz[*a*]anthracen-7-yl radical (**21**), but it is believed to arise from the initial rearrangement product(s) by subsequent skeletal reorganizations.

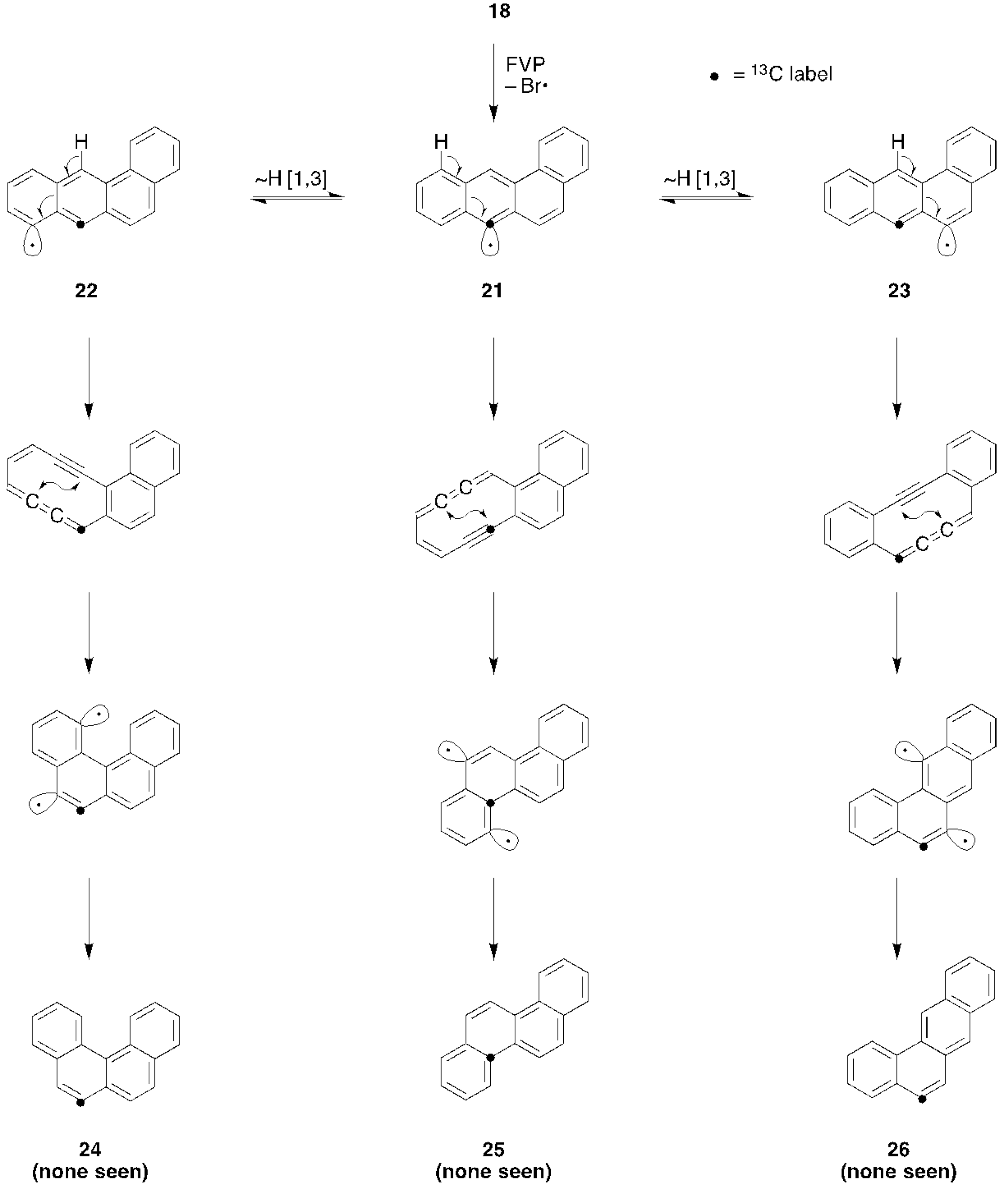
Scheme 16



18 **19** **20**
^{13}C-labeled

Scheme 17 (next page) shows the expected fragmentation pathways available to the 7-[^{13}C]benz[*a*]anthracen-7-yl radical (**21**). The absence of hydrocarbons **24**, **25**, and **26** among the FVP products strongly suggests that the reactive intermediates derived from the 7-[^{13}C]benz[*a*]anthracenyl radical **21** (and from its 1,3-hydrogen shift isomers, **22** and **23**) find their way to the acefluoranthrylene ring system (**20**) more readily than they scavenge hydrogen atoms to give hydrocarbons **24**, **25**, and **26**.

Scheme 17



The detailed pathway(s) by which 7-[^{13}C]benz[*a*]anthracen-7-yl radical (**21**) is transformed into acefluoranthrylene (**20**) remain a matter of speculation at this point, but whatever mechanistic scheme is proposed must account for the observed distribution of the ^{13}C label in **20**. Despite this remaining uncertainty, these results provide further evidence for the rupture of transannular bonds in acene radicals.

8. Ongoing Collaborations and Results to Date

In collaboration with Professor P. E. Georghiou at Memorial University in St. Johns, Newfoundland, we are studying the host-guest chemistry of C_{60} and higher fullerenes with calix[4]azulene and with an octaphenylcalix[4]azulene that was recently synthesized for the first time in our laboratory.

In collaboration with Professor R. Fasel at EMPA in Zurich, Switzerland, we recently found conditions to transform pentabenzocorannulene to an end-cap for [5,5] carbon nanotubes by surface catalyzed cyclodehydrogenation on a Pt(111) surface under ultrahigh vacuum conditions. Further experiments are now underway to try to grow uniform [5,5] carbon nanotubes from these metal-bound templates. Samples of pentabenzocorannulene have also been sent to Professor K. Itami (Nagoya University, Japan), Professor N. Martin (Universidad Complutense de Madrid, Spain), and Professor C. Zhao (University of Southern California), who are pursuing similar experiments. Professors Itami and Zhao are also exploring possible methods for the metal-free growth of [5,5] carbon nanotubes from a $C_{50}H_{10}$ hemispherical nanotube end-cap that we synthesized several years ago.

In collaboration with Professor J. Harper at the University of New South Wales in Sydney, Australia, we developed a versatile new route for the synthesis of substituted fluorenones.

In collaboration with Professor T. Kawase at the University of Hyogo, Japan, we discovered exceptionally large ion-pairing effects on the tropicity of the bicyclo[6.3.0]undecapentaenyl anion, the next higher homolog of the indenyl anion. The same collaboration also uncovered unusual ambiphilic properties of the aromatic carbene bicyclo[6.3.0]undeca-1(11),2,4,6,8-pentaen-10-ylidene.

In collaboration with Prof. R. Le Parc at the University of Montpellier, France, we gained new insights on the vibrational dynamics of corannulene.

In collaboration with Professor M. Marcaccio at the University of Bologna in Italy, we are about to publish the first results of our ongoing investigation into the nature of an unusual polymer formed by electrochemical oxidation of corannulene.

In collaboration with Professor M. A. Petrukhina at the University at Albany, SUNY, we are nearing completion of a comprehensive study on the X-ray crystal structures of all the benzocorannulenes, including the parent corannulene, mono-, di-, tri-, tetra-, and pentabenzocorannulene.

In collaboration with Professor R. Shenhar at the Hebrew University, Jerusalem, Israel, we studied the unprecedented extended supramolecular oligomerization of anionic 1,4-dicorannulenylbenzene and the corresponding branched supramolecular oligomerization 1,3,5-tricorannulenylbenzene.

In collaboration with Professor A. Wakamiya at Kyoto University in Japan, we developed novel hole-transporting materials based on substituted azulenes for use in perovskite solar cells. New record efficiencies were achieved.

Publications and Presentations Since July 1, 2012:

1. Refereed journal articles and book chapters

§Publications for which research was funded entirely by this DOE grant.
‡Publications for which research was funded partially by this DOE grant.
†Publications for which research was funded entirely by other agencies.

- "A Short, Rigid, Structurally Pure Carbon Nanotube by Stepwise Chemical Synthesis," Scott, L. T.; Jackson, E. A.; Zhang, Q.; Steinberg, B. D.; Bancu, M.; Li, B. *J. Am. Chem. Soc.* **2012**, *134*, 107-110.‡

- "Corannulene and its Penta-*tert*-Butyl Derivative Co-crystallize 1:1 with Pristine C_{60}-Fullerene," Dawe, L. N.; AlHujran, T.; Tran, H.-A.; Mercer, J. I.; Jackson, E. A.; Scott, L. T.; Georghiou, P. E. *Chem. Commun.* **2012***, 48*, 5563-5565 (highlighted on the cover).§

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- "Special Electronic Structure and Extended Supramolecular Oligomerization of Anionic 1,4-Dicorannulenylbenzene," Eisenberg, D.; Quimby, J. M.; Ho, D.; Lavi, R.; Benisvy, L.; Scott, L. T.; Shenhar, R. *Eur. J. Org. Chem.* **2012**, 6321-6327 (highlighted on the cover)§

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- “Hole-Transporting Materials with a Two-Dimensionally Expanded π-System Around an Azulene Core for Efficient Perovskite Solar Cells,” Nishimura, H.; Ishida, N.; Shimazaki, A.; Wakamiya, A.; Saeki, A.; Scott, L. T.; Murata, Y. *J. Am. Chem. Soc.* **2015**, *137*, 15656-15659.‡ http://dx.doi.org/10.1021/jacs.5b11008

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- “Exotic Chemistry and Rational Organic Syntheses at 1000 °C,” Scott, L. T. *J. Org. Chem.* **2016**, *81*, 11535-11547.‡ (invited *PERSPECTIVE* - highlighted on the cover). http://pubs.acs.org/doi/abs/10.1021/acs.joc.6b02113

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- “Bicyclo[6.3.0]undeca-1(11),2,4,6,8-pentaen-10-ylidene: An aromatic carbene having ambiphilic properties,” Ishikawa, H.; Nishida, J.; Jones, J. W., Jr., Scott, L. T.; Kawase, T. *ChemPlusChem* **2017**, published on the web March 22, 2017.‡ http://onlinelibrary.wiley.com/doi/10.1002/cplu.201700069/full

2. Book reviews (solicited by the editor and published but not refereed)

- "Aromaticity and Other Conjugation Effects," Gleiter, R.; Haberhauer, G., Wiley-VCH: Weinheim. 2012; review by Scott, L. T.; Cho, H. Y.; Eliseeva, M. N.; Jackson, E. A.; Tanaka, T.; Tanikawa, T. *Angew. Chem. Int. Ed.* **2013**, *52*, 2-3.

3. Presentations at professional meetings, universities, and companies

- Contributed conference paper: "Direct C–H Arylation of Polycyclic Aromatic Hydrocarbons Through Palladium Catalysis," Kawasumi, K.; Kajino, T.; Mochida, K.; Segawa, Y.; Scott, L. T.; Itami, K. presented by K. Kawasumi at the Nagoya University Global COE International Symposium & 7th and 8th Yoshimasa Hirata Memorial, Nagoya, Japan, November 2011

- Contributed conference paper: "Pd-catalyzed Direct Arylation of Polycyclic Aromatic Hydrocarbons," Kawasumi, K.; Mochida, K.; Segawa, Y.; Scott, L. T.; Itami, K. award presentation by K. Kawasumi at the 92nd Annual Meeting of Chemical Society of Japan, Kanagawa, Japan, March 2012

- Contributed conference paper: "Mechanistic Investigations of Aryl–Aryl Bond Fragmentation Reactions," Cho, H. Y.; Scott, L. T. presented by H. Y. Cho at the American Chemical Society National Meeting, San Diego, CA, March 2012. (abstract ORGN 414)

- Contributed conference paper: "Synthesis and Reactions of a Highly-Strained Open Geodesic Polyarene," Cho, H. Y.; Spisak, S. N.; Petrukhina, M. A.; Scott, L. T. presented by H. Y. Cho at the American Chemical Society National Meeting, San Diego, CA, March 2012 (abstract ORGN 848)

- Contributed conference paper: "Direct π-extension of PAHs by C–H Functionalization," Kawasumi, K.; Kajino, T.; Mochida, K.; Segawa, Y.; Scott, L. T.; Itami, K. presented by K. Kawasumi at the Münster Symposium on Cooperative Effects in Chemistry, Münster, Germany, May 4, 2012

- Contributed conference paper: "Direct π-extension of PAHs by C–H Functionalization," Kawasumi, K.; Kajino, T.; Mochida, K.; Segawa, Y.; Scott, L. T.; Itami, K. presented by K. Kawasumi at the 13th IRTG Münster-Nagoya Joint Symposium, Münster, Germany, May 7, 2012

- Contributed conference paper: "Precursors for the Chemical Synthesis of a C_{6v}-Symmetric [6,6] Carbon Nanotube," Will, K. R.; Wilson, B. G.; Greene, A. K.; Scott, L. T. (presented by K. R. Will at the American Chemical Society National Meeting, Philadelphia, PA, August 2012 (abstract ORGN 191)

- Contributed conference paper: "Synthesis of a 21-Ring Carbon Nanotube End-Cap and a 26-Ring Warped Graphene Segment from Corannulene," Zhang, Q.; Jackson, E. A.; Kawasumi, K.; Itami, K.; Scott, L. T. presented by Q. Zhang at the American Chemical Society National Meeting, Philadelphia, PA, August 2012 (abstract ORGN 368)

- Contributed conference paper: “Synthesis of Fully Aromatic Linear Type Graphene Ribbons Through Diels-Alder Cycloaddition of Dimesitylbisanthene and *p*-Benzoquinone and Aromatization,” Tanikawa, T.; Fort, E. H.; Jeffreys, M. S.; Scott, L. T. presented by T. Tanikawa at the American Chemical Society National Meeting, Philadelphia, PA, August 2012 (abstract ORGN 370)

- Contributed conference paper: “Synthesis of Benzocorannulenes Toward a Carbon Nanotube End-Cap,” Tanaka, T.; Smith, N. J.; Scott, L. T. presented by T. Tanaka at the 23rd Symposium on Physical Organic Chemistry, Kyoto, Japan, September 2012

- Contributed conference paper: “Creation of Novel Nanographene by Pd-catalyzed Direct Arylation,” Kawasumi, K.; Segawa, Y.; Scott, L. T.; Itami, K. presented by K. Kawasumi at the 23rd Symposium on Physical Organic Chemistry, Kyoto, Japan, September 2012

- Invited conference paper: “Chemical Methods for the Synthesis of Soluble Graphene Ribbons,” Tanikawa, T.; Scott, L. T., presented by T, Tanikawa at the Crystal & Graphene Science Symposium-2012, Waltham, Massachusetts, September 5-6, 2012

- Invited chemistry department research lecture presented by L. T. Scott: Institute for Advanced Studies in Nanoscience, Madrid, Spain (IMDEA-Nanoscience), September 10, 2012

- Invited chemistry department research lecture presented by L. T. Scott: Institute of Chemical Research of Catalonia (ICIQ - Institut Català d'Investigació Química), Tarragona, Spain, September 14, 2012

- Invited chemistry department research lecture presented by L. T. Scott: University of Bordeaux, France, September 21, 2012

- Invited conference paper: “Chemical Methods for Synthesizing Fullerenes and Carbon Nanotubes of Predefined Structure,” presented by L. T. Scott at the German Chemical Society National Organic Symposium (GDCh ORCHEM-2012), Weimar, Germany, September 2012

- Invited conference paper: “Chemical Methods for Synthesizing Fullerenes and Carbon Nanotubes of Predefined Structure,” presented by L. T. Scott at the Fifth Peking University-Eli Lilly Symposium of Organic Chemistry, Peking University, Beijing, China, October 2012

- Invited chemistry department research lecture presented by L. T. Scott: Shaanxi Normal University, Xi’An, China, October 23, 2012

- Invited chemistry department research lecture presented by L. T. Scott: Fudan University, Shanghai, China, October 25, 2012

- Invited chemistry department research lecture presented by L. T. Scott: University of Houston, Texas, November 13, 2012

- Invited chemistry department research lecture presented by L. T. Scott: Rice University, Houston, Texas, November 14, 2012

- Invited chemistry department research lecture presented by L. T. Scott: University of Colorado, Boulder, November 16, 2012

- Invited chemistry department research lecture presented by L. T. Scott: University of Ottawa, Canada, December 5, 2012

- Contributed conference paper: “Pushing the Ir-Catalyzed C-H Polyborylation of Aromatic Compounds to Maximum Capacity by Exploiting Reversibility,” Eliseeva, M. N; Scott, L. T., presented by M. N. Eliseeva at the Annual Meeting of the American Association for the Advancement of Science, Boston, Massachusetts, February 14-18, 2013

- Contributed conference paper: “A Missing Link between Classic Flat Aromatics and Novel Fullerenes,” Cho, H. Y.; Ansems, R. B. M.; Scott, L. T. presented by H. Y. Cho at the Annual Meeting of the American Association for the Advancement of Science, Boston, Massachusetts, February 14-18, 2013

- Contributed conference paper: “Molecular Templates with Potential for the Selective Production of Single Walled Carbon Nanotubes,” Jackson, E. A.; Zhang, Q.; Scott, L. T. presented by E. A. Jackson at the Annual Meeting of the American Association for the Advancement of Science, Boston, Massachusetts, February 14-18, 2013

- Contributed conference paper: “Synthesis of Graphene Nanoribbons by Diels-Alder Cycloadditions of Dimesitylbisanthene and p-Benzoquinone Followed by Aromatization,” Tanikawa, T.; Fort, E. H.; Jeffreys, M. S.; Scott, L. T. presented by T. Tanikawa at the Annual Meeting of the American Association for the Advancement of Science, Boston, Massachusetts, February 14-18, 2013

- Invited conference paper: “Diels-Alder Cycloadditions in the Bay Regions of Large Polycyclic Aromatic Hydrocarbons,” Tanikawa, T.; Fort, E. H.; Jeffreys, M. S.; Scott, L. T., presented by L. T. Scott at the Award Symposium for Research at an Undergraduate Institution, American Chemical Society National Meeting, New Orleans, Louisiana, April 2013 (abstract ORGN 10)

- Contributed conference paper: “An Electrochemical Reaction Pathway for the Generation of Graphene-Like Films and Self-Assembled Nanographenes,” Valenti, G.; Scott, L. T.; Marcaccio, M.; Fontanesi, C.; Paolucci, F. Presented by M. Marcaccio at the 223rd Meeting of the Electrochemical Society, Toronto, Canada, May 2013

- Invited chemistry department research lecture presented by L. T. Scott: University of Bologna, Italy, May 31, 2013

- Invited chemistry department research lecture presented by L. T. Scott: University of Salerno, Italy, June 7, 2013

- Invited chemistry department research lecture presented by L. T. Scott: Charles University, Prague, Czech Republic, June 10, 2013

- Invited chemistry department research lecture presented by L. T. Scott: University of Warsaw, Poland, June 13, 2013

- Contributed conference paper: “Exact and Quantitative Analysis of Deuterated Pyrene: A New Method for the Rapid, Convenient Hydrogen-Deuterium Exchange of Polycyclic Aromatic Hydrocarbons,” Domin, M. A.; Greene, A. K.; Scott, L. T.; Gu, M.; Wang, Y. Presented by M. Domin at the 61st Annual Conference of the American Society for Mass Spectrometry (ASMS-2013), Minneapolis, Minnesota, June 2013

- Invited plenary lecture: “Can Organic Chemists Deliver Structurally Uniform Fullerenes and Carbon Nanotubes by Custom Synthesis?” American Chemical Society National Organic Symposium (NOS-2013), Seattle, Washington, June 2013

- Contributed conference paper: “Syntheses of Tribenzo[*a,d,j*]- and Tetrabenzo[*a,d,g, j*]corannulenes by Intramolecular Palladium-Catalyzed Arylation Reactions,” Tanaka, T.; Miyake, H.; Pohako-Esko, K.; Smith, N. J.; Scott, L. T. Presented by T. Tanaka at the IUPAC 15th International Symposium on Novel Aromatic Compounds (ISNA-15), Taipei, Taiwan, July/August 2013 (poster A-56)

- Contributed conference paper: “Synthesis of a Grossly Warped Graphene Segment from Decaphenylcorannulene,” Zhang, Q.-Y.; Kawasumi, K.; Segawa, Y.; Itami, K.; Scott, L. T. Presented by Q.-Y. Zhang at the IUPAC 15th International Symposium on Novel Aromatic Compounds (ISNA-15), Taipei, Taiwan, July/August 2013 (poster A-62)

- Contributed conference paper: “Synthesis of Graphene Nanoribbons by Diels-Alder Cycloaddition Reactions at Bay Regions of Dimesitylbisanthene,” Tanikawa, T.; Fort, E. H.; Jeffreys, M. S.; Scott, L. T. Presented by T. Tanikawa at the IUPAC 15th International Symposium on Novel Aromatic Compounds (ISNA-15), Taipei, Taiwan, July/August 2013 (poster A-67)

- Contributed conference paper: “Direct C–H Arylation of Polycyclic Aromatic Hydrocarbons through Palladium Catalysis,” Segawa, Y.; Kawasumi, K.; Mochida, K.; Fujikawa, T. Kajino, T.; Zhang, Q.-Y.; Scott, L. T.; Itami, K. Presented by Y. Segawa at the IUPAC 15th International Symposium on Novel Aromatic Compounds (ISNA-15), Taipei, Taiwan, July/August 2013 (poster A-78)

- Contributed conference paper: “Synthesis of Pentabenzo[*a,d,g,j,m*]corannulene toward a 40-Carbon End-cap,” Tanaka, T.; Scott, L. T. Presented by T. Tanaka at the IUPAC 15th International Symposium on Novel Aromatic Compounds (ISNA-15), Taipei, Taiwan, July/August 2013 (poster B-52)

- Contributed conference paper: “Synthesis of Pentabenzocorannulene. Toward a Carbon Nanotube $C_{40}H_{10}$ End-cap,” Miyake, H.; Tanaka, T.; Hashimoto, S.; Põhako-Esko, K.; Scott, L. T. Presented by H. Miyake at the 24th Symposium on Physical Organic Chemistry, Tokyo, Japan, September 2013

- Invited symposium lecture: “High Temperature Chemistry of Aromatic Hydrocarbons,” Storch Award in Fuel Science Symposium, American Chemical Society National Meeting, Indianapolis, Indiana, September 2013 (abstract ENFL 237)

- Invited plenary lecture: "Can Organic Chemists Deliver Structurally Uniform Fullerenes and Carbon Nanotubes by Custom Synthesis?" 2nd Erlangen Symposium on Synthetic Carbon Allotropes, Erlangen, Germany, September 2013

- Invited chemistry department research lecture presented by L. T. Scott: University of Heidelberg, Germany, October 4, 2013

- Invited chemistry department research lecture presented by L. T. Scott: Columbia University, New York, January 23, 2014

- Invited chemistry department research lecture presented by L. T. Scott: Universidad Autónoma Metropolitana-Iztapalapa, Mexico City, January 29, 2014

- Contributed conference paper: "Synthesis of pentabenzocorannulene: Toward a $C_{40}H_{10}$ carbon nanotube end-cap," Hashimoto, S.; Miyake, H.; Tanaka, T.; Bhola, R.; Pohako-Esko, K.; Scott, L. T. Presented by S. Hashimoto at the American Chemical Society National Meeting, Dallas, Texas, March 2014 (abstract ORGN 24)

- Contributed conference paper: "Syntheses of benzocorannulenes," Bhola, R.; Hashimoto, S.; Tanaka, T.; Miyake, H.; Pohako-Esko, K.; Scott, L. T. Presented by R. Bhola at the American Chemical Society National Meeting, Dallas, Texas, March 2014 (abstract ORGN 227)

- Contributed conference paper: "Acene-to-phenacene skeletal isomerizations at high temperatures in the gas phase," Kamath, A.; Necula, A.; Scott, L. T. Presented by A. Kamath at the American Chemical Society National Meeting, Dallas, Texas, March 2014 (abstract ORGN 640)

- Contributed conference paper: "Bottom-up metal-free synthesis of nearly pure semiconducting carbon nanotubes," Bhola, R.; Liu, B.; Jackson, E. A.; Zhou, C.; Scott, L. T. Presented by R. Bhola at the American Chemical Society National Meeting, Dallas, Texas, March 2014 (abstract ORGN 726)

- Invited lecture: "Can Organic Chemists Deliver Structurally Uniform Fullerenes and Carbon Nanotubes by Custom Synthesis?" Philadelphia Organic Chemists' Club Symposium, April 17, 2014.

- Contributed conference paper: "Supramolecular Chemistry of Calixazulenes and Calixnaphthalenes: Binding and Computational Studies," Georghiou, P. E.; Rahman, S.; Zein, A.; Thompson, D. W.; Strange, T.; Nishimura, H.; Eliseeva, M. N.; Scott, L. T. Presented by P. E. Georghiou at the 22nd IUPAC Conference on Physical Organic Chemistry, Ottawa, Canada, August 2014

- Contributed conference paper: "Development of Hole-Transporting Materials Using Quasiplanar Structure as a Key Skeleton," Nishimura, H.; Endo, M.; Wakamiya, A.; Scott, L. T.; Murata, Y. Presented by H. Nishimura at the 25th Symposium on Physical Organic Chemistry, Sendai, Japan, September 2014

- Invited plenary lecture: 25th Fundación Ramón Areces Scientific Symposium on Chemistry: Answers for a Better World, Madrid, Spain, October 2014

- Invited plenary lecture: 1st International Symposium on the Synthesis and Application of Curved Organic π-Molecules and Materials, Kyoto, Japan, October, 2014

- Contributed conference paper: "Development of Hole-Transporting Materials Using Quasiplanar Structure as a Key Skeleton," Nishimura, H.; Endo, M.; Wakamiya, A.; Scott, L. T.; Murata, Y. Presented by H. Nishimura at the 1st International Symposium on the Synthesis and Application of Curved Organic π-Molecules and Materials, Kyoto, Japan, October, 2014

- Invited chemistry department research lecture presented by L. T. Scott: Nagoya University, Japan, October 22, 2014

- Invited plenary lecture: 4th International Symposium on Element Innovation, Gunma University, Kiryu, Japan, October, 2014

- Invited chemistry department research lecture presented by L. T. Scott: Miami University, Oxford, Ohio, November 13, 2014

- Invited chemistry department research lecture presented by L. T. Scott: University of Cincinnati, Cincinnati, Ohio, November 14, 2014

- Invited chemistry department research lecture presented by L. T. Scott: West Virginia University, Morgantown, West Virginia, January 28, 2015

- Contributed conference paper: "Synthesis of Carbon Nanotubes by Means of 'Molecular Template Epitaxial Growth' Approach," Hong, L.; Takakura, A.; Scott, L. T.; Miyauchi, Y.; Itami, K. Presented by L. Hong at the 48th Fullerenes-Nanotubes-Graphene Symposium (FNTG48), Tokyo, Japan, February 2015

- Invited chemistry department research lecture presented by L. T. Scott: University of South Florida, St. Petersburg, Florida, February 23, 2015

- Contributed conference paper: "Development of Hole-Transporting Materials toward Efficient Perovskite-Based Solar Cells," Nishimura, H.; Maruyama, N.; Endo, M.; Wakamiya, A.; Scott, L. T.; Murata, Y. Presented by H. Nishimura at the 95th Annual meeting of the Chemical Society of Japan, Chiba, Japan, March 2015

- Invited chemistry department research lecture presented by L. T. Scott: Marquette University, Milwaukee, Wisconsin, March 27, 2015

- Invited chemistry department research lecture presented by L. T. Scott: San Francisco State University, San Francisco, California, May 8, 2015

- Invited plenary lecture: IUPAC Sixteenth International Symposium on Novel Aromatic Compounds (ISNA-16), Madrid, Spain, July 2015: "The Benzocorannulenes" (abstract PL10).

- Contributed conference paper: "Development of New Hole-Transporting Materials Containing Quasiplanar Skeleton for Perovskite-Based Solar Cells," Nishimura, H.; Maruyama, N.; Endo, M.; Wakamiya, A.; Scott, L. T.; Murata, Y. presented by H. Nishimura at the IUPAC Sixteenth International Symposium on Novel Aromatic Compounds (ISNA-16), Madrid, Spain, July 2015

- Contributed conference paper: "An Electrochemical Reaction Pathway for the Generation of Graphene-Like Films and Self-Assembled Nanographenes," Marcaccio, M.; Ussano, E.; Valenti, G.; Scott, L. T.; Fontanesi, C.; Paolucci, F. presented by M. Marcaccio at the National Meeting of the American Chemical Society, Boston, Massachusetts, August 2015 (abstract ORGN 803)

- Contributed conference paper: "Transannular Bond Scissions in *Cata*-Condensed PAH Radicals at High Temperatures in the Gas Phase," Kamath, A.; Necula, A.; Hill, T. J.; Scott, L. T. presented by L. T. Scott at the International Symposium on Polycyclic Aromatic Compounds (ISPAC-2015), Bordeaux, France, September 2015

- Invited chemistry department research lecture presented by L. T. Scott: University of Basel, Switzerland, September 2015

- Invited lecture: Symposium on Nano and Supramolecular Chemistry held in conjunction with the IX International Congress on Chemical Sciences, Technology and Innovation (QUIMICUBA 2015), Havana, Cuba, October 2015: "Growing Carbon Nanotubes from Synthetic Organic End-Caps"

- Invited plenary lecture: Symposium on Chemistry of Nanocarbons – Fullerenes, Carbon Nanotubes, Nanographenes and Related Materials, held in conjunction with PACIFICHEM 2015, Honolulu, Hawaii, December 2015: "Growing Carbon Nanotubes from Organic End-caps."

- Invited plenary lecture: Symposium on Graphene, held in conjunction with PACIFICHEM 2015, Honolulu, Hawaii, December 2015: "Warped Nanographenes and Soluble Graphene Nanoribbons."

- Contributed conference paper: "Hole-Transporting Materials with a Two-Dimensionally Expanded **π**-System for Efficient Perovskite Solar Cells," Wakamiya, A.; Nishimura, H.; Ishida, N.; Shimazaki, A.; Saeki, A.; Scott, L. T.; Murata, Y. presented by Atsushi Wakamiya at the Institute for Chemical Research International Symposium (ICRIS-2016), Kyoto, Japan, March 2016:

- Invited plenary lecture: International Symposium on π-System Figuration, Saitima, Japan, April 2016: "Polyarene Bowls, Baskets, Balls, Sheets, and Tubes"

- Invited plenary lecture: 70th Fujiwara Symposium on Physical Organic Chemistry, Fukuoka, Kyushu, Japan, April 2016: "Polyarene Bowls, Baskets, Balls, Sheets, and Tubes"

- Invited lecture: 23rd International Symposium on Physical Organic Chemistry (ICPOC-23), Sydney, Australia, July 2016: "Growing Carbon Nanotubes From Synthetic Organic End-Caps"

- Award lecture: A. C. Cope Scholar Award Symposium, American Chemical Society National Meeting, Philadelphia, August 2016: "Unprecedented Organic Reactions and Rational Synthesis at 1000 °C" (abstract ORGN 370)

- Invited research lecture: ExxonMobil Corporate Strategic Research Labs, Annandale, NJ, March 2017

- Invited plenary lecture: R. C. Haddon Memorial Symposium, Univ. of California, Riverside, April 2017: "Growing Carbon Nanotubes from Synthetic Organic End-Caps"

Special Recognitions, Positions, Honors, and Awards Since July 1, 2012:

- Named a Fellow of the American Chemical Society, 2012

- Member of the editorial advisory board for *The Journal of Organic Chemistry*, 2011 - 2015

- Member of the editorial advisory board for *Polycyclic Aromatic Compounds*, 2004 - present

- LU JIAXI LECTURE, Xiamen University, China, 2012

- Chair, Division of Organic Chemistry of the American Chemical Society, 2013

- Co-organized the first American Chemical Society Symposium on Graphene Chemistry at the ACS National Meeting in New Orleans, Louisiana, April 2013

- Member of the International Advisory Board and session chair for the IUPAC Fifteenth International Symposium on Novel Aromatic Compounds, Taipei, Taiwan, July/August 2013

- Organizer and chair of the Symposium for the American Chemical Society Award for Creative Work in Synthetic Organic Chemistry at the ACS National Meeting in New Orleans, Louisiana, April 2013

- Appointed Professor of Chemistry Emeritus, Boston College, 2014

- Appointed Visiting Professor of Chemistry, Nagoya University, 2014

- Appointed Adjunct Professor of Chemistry, University of Nevada, Reno, 2014

- Co-organizer of the International Symposium "From Carbon-Rich Molecules to Carbon-Based Materials" Mazagan, Morocco, September 2014

- Session chair at the 1st International Symposium on the Synthesis and Application of Curved Organic π-Molecules and Materials, Kyoto, Japan, October, 2014

- Organizer and chair of the Symposium for the American Chemical Society James Flack Norris Award in Physical Organic Chemistry at the ACS National Meeting in Denver, Colorado, March 2015

- Session chair at the Gordon Research Conference on Physical Organic Chemistry, Plymouth, New Hampshire, June 2015
- Member of the International Advisory Board for the IUPAC 16th International Symposium on Novel Aromatic Compounds, Madrid, Spain, July 2015
- Session chairman for the Symposium on Nano and Supramolecular Chemistry held in conjunction with the IX International Congress on Chemical Sciences, Technology and Innovation (QUIMICUBA 2015), Havana, Cuba, October 2015
- American Chemical Society Cope Scholar Award, 2016