

A laser desorption ionization mass spectrometry investigation of triarylboranes and tri-9-anthrylborane photolysis products

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Abstract

Laser desorption ionization (LDI) mass spectra have been obtained for the photolysis products of tri-9-anthrylborane (TAB) in the solvents toluene, cyclohexene, and tetrahydrofuran; and for the solid triarylboranes: TAB, trimesitylborane (TMB), and tri-(2,6-dimethylphenyl)borane (TXyB). The major single solution photolysis product of TAB is 9,9'-dianthryl. Other products are rationalized in terms of an anthrylborylene intermediate (AnthB:). LDI mass spectrometry of the triarylboranes yields molecular ions in good abundance, providing a simple and selective method of characterization. Fragmentation patterns in some cases are interpreted in terms of photochemical reactions prior to ionization.

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1. Introduction

In the process of closing down his laboratory, one of us (B.G.R.) made the serendipitous discovery, that in a cyclohexane solution of tri-9-anthrylborane or TAB, **1**, exposed for over a year to the ambient fluorescent light of the laboratory, the ultraviolet spectrum of TAB had been replaced with that of 9-(9'-anthryl)anthracene or dianthryl in almost quantitative yield. This reaction had been previously overlooked, because, as we have subsequently found, dianthryl itself is photochemically destroyed by the usual light irradiation sources even when the light is filtered through Pyrex. The discovery that the photolysis of solutions of TAB yields dianthryl as a major product raises the exciting possibility that the remaining fragment, 9-anthrylborylene (AnthB:), was also produced.

This result has precedence. The photolysis of tri-1-naphthylborane (TNB) in hydrocarbon solvents does form 1,1'-dinaphthyl in 5–10% yields [1,2]. There is disagreement [2] whether the analysis of the products of TNB photolysis in cyclohexene supports the intermediacy of naphthylborylene as suggested by Ramsey and Anjo [1]. It was agreed that a major pathway in the solution photochemistry of TNB is simple fragmentation of TNB into neutral naphthyl and dinaphthylboryl radicals [1,2].

Studies of arylborane photochemistry over the years have been sparse. An early study of the photolysis of triphenylborane in cyclohexane by Williams et al. [3] found no hydrocarbon products; photolysis in methanol did yield small amounts of biphenyl, attributed to photochemistry of the triphenylborane methanol complex. This photochemistry is analogous to the extensively studied [4] photolysis of the tetraphenylborate anion to form biphenyl and products from another carbene analog, $\text{Ph}_2\text{B:}$. Along similar lines, heterolytic boron carbon bond cleavage has been reported in the photolysis of tribenzylborane solvent complexes in ether/methanol

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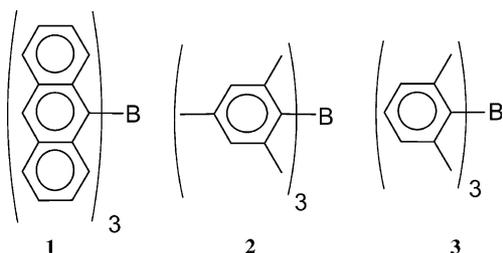
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mixtures where high yields of toluene were attributed to formation of an intermediate benzyl anion, which is then protonated by methanol [5]. The observation by Hancock and Dickson [6] of alkyl boron carbon bond cleavage in the photochemistry of aminoboranes (alkyl-(*N*-methylanilino)-phenylboranes) seems to us an interesting extension of the idea that photochemical boron carbon bond cleavage is facilitated by negative charge density at boron.

The first UV absorption maximum in the spectra of triarylboranes such as triphenyl and trinaphthyl borane is an intense broad band in the region between 280 and 355 nm. These transitions [7] have been characterized as intramolecular charge transfer transitions. Neglecting configuration interaction, the transition promotes an electron from a highest occupied π molecular orbital (HOMO), localized on the aromatic rings, to a predominantly boron 2p lowest unoccupied orbital (LUMO).

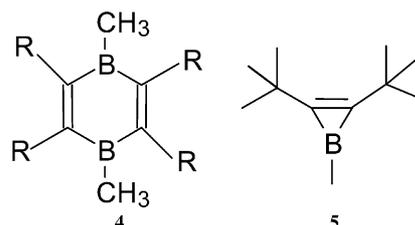
We have utilized LDI mass spectrometry (MS) [8] to examine the products of the photochemical reaction of TAB in several different solvents: cyclohexene, toluene, and tetrahydrofuran. The LDI method illustrates the advantage of selectively ionizing only those reaction products, from a complex mixture, absorbing at the laser wavelength of 337 nm – in our case anthracene or other aryl chromophores.

To our surprise, there appear to be no reports in the literature of a systematic study of the mass spectra of arylboranes or even reports of the mass spectra of such common individual compounds such as triphenylborane. This may be at least in part due to the fact that, in our own experience, electron ionization MS of triarylboranes do not exhibit parent ion peaks. We have therefore continued our LDI studies on unreacted solids of TAB, trimesitylborane (TMB) **2**; and tri-(2,6-dimethylphenyl)borane (TXyB) **3**, both to extend our understanding of the behavior of arylboranes under the conditions of LDI MS and to look for evidence of laser induced photochemistry in the melt or gas phase.

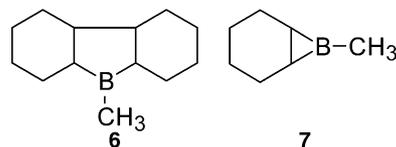


Since the results of LDI of TAB photolysis products, and the triarylboranes: TAB, TXyB, and TMB are discussed in terms of photochemical reactions producing arylborylenes (ArB), a brief review of the current state

of “organo-borylene” chemistry is provided. Although “borylene” products have been reported in a number of reactions, there is some question if free borylenes, RB:, are always actual intermediates. Attempts to demonstrate the formation, of MeB: in a mixture of MeBBr₂, potassium-graphite laminate (C₈K) and benzene, by trapping the borylene with alkynes has met with ambiguous results. For example, efforts to reproduce the reported [9] trapping of MeB: with alkynes, followed by dimerization of the borirene to 1,4-dibora-2,5-cyclohexadienes, **4**, have not been successful [10]. Eisch and Becker [11] have reported the formation of the aromatic borirene, **5**, utilizing di-*t*-butylacetylene as the trapping agent, although the structure was assigned solely on mass spectral fragmentation data.



The reaction of MeBBr₂ and C₈K with cyclohexene in refluxing benzene yields as the major product the boratricyclotridecane, **6** [12]. Its formation was rationalized as an allowed $\pi 2s + \sigma 2a$ concerted addition product of **7** to a second molecule of cyclohexene. Boracyclopropanes are boron analogs of the cyclopropylation, which is well known not to be a minimum on the potential energy surface of a C₃H₅⁺ ion. And although both semi-empirical and *ab initio* calculations [13] do indicate that a boracyclopropane is an energy minimum, it may be overly optimistic to assume that they would survive in refluxing benzene.



The product might be formed through a reaction initiated by a radical boron anion. Haloboration mechanisms have also been suggested [9,10] as alternatives. In any case, the “methylborylene” generated by MeBBr₂ reaction with C₈K or NaK does not undergo addition to C=C aromatic bonds, or C–H bonds except in benzene chromium tricarbonyl and ferrocene [14].

There have been reported attempts with inconclusive results, to generate C₆H₅B: from C₆H₅BBr₂ with K in petroleum ether [15] or Li in THF [16] and to then trap

the borylene with diphenylacetylene. The early reported success of Joy et al. [15] could not be reproduced by Eisch and Gonsior [16].

More recently, Grigsby and Power [17] reported that the reaction of 2,5-dimesityl-phenyl-boron dibromide with lithium or C_8K in diethylether or benzene gave products of intramolecular borylene insertion into the carbon–carbon bond of the nearby methyl group. The resulting product was a methylborafluorene derivative. This is the only example reported thus far of what might be an organo-borylene carbon–carbon bond insertion reaction.

Strikingly, different results are obtained [18] from reactions of the diisopropylaminoboron difluoride, $(Me_2CH)_2NBF_2$, Na/K system in 1,2-dimethoxyethane (DME) with toluene, *m*-xylene, benzene, and naphthalene. The products, whose structures in the case of toluene and xylene were determined by X-ray crystallography, are the result of multiple insertions of the $(Me_2CH)_2NB$: fragment between the aromatic ring carbons, forming products in which the borons are tricoordinate.

2. Experimental

2.1. Photolysis reactions

After a 250 ml cyclohexane solution of tri-9-anthrylborane was left exposed to laboratory fluorescent lighting for over one year, the charge transfer spectrum of TAB was largely replaced with that of 9,9'-dianthryl: λ_{max} nm, (absorbance), 391 (0.6), 370 (0.5), 350 (0.3), 334 (0.32). Solvent reduction to 20 ml, followed by chromatography on neutral alumina, gave a white crystalline hexane eluent fraction, whose ultraviolet spectrum [19] was that of 9,9'-bianthryl and whose LDI mass spectrum consisted of a mass at 354.13 u with no other mass greater than 0.5% abundance between 100 and 2500 u.

Subsequent photochemical reactions of TAB in toluene, cyclohexene, and tetrahydrofuran (THF) were run under nitrogen in 50–60 ml of solvent, which had been purged with nitrogen or argon for 30 min. The reaction vessel was a standard 100 ml one necked Pyrex round bottom flask with a side arm Teflon stopcock. The light source was either a General Electric (GE) 75 W Grow Light, for plants, or a water cooled Hanovia 450 W medium pressure quartz mercury vapor lamp. The emission from the Hanovia lamp was filtered through both a Pyrex sleeve and the body of a 500 ml Ace Glass Pyrex photochemical reaction vessel, limiting sample irradiation to wavelengths longer than 280 nm. A typical final reaction time in front of the Hanovia lamp would be 12–16 h. In some runs, the reactions were followed by withdrawing 5 ml aliquot samples for ultraviolet spectra analysis.

In toluene, 2–5 mg of TAB was photolyzed under nitrogen, for 2–3 days in front of the GE Grow Light

until the absorbance of the 474 nm CT maximum decreased to less than one tenth its original value. Photolysis of five mg of TAB in THF was carried out for three days under the GE Grow Light, after which time the 474 nm CT band of TAB was reduced to a shoulder on the side of a new maximum at 436 nm. The photolysis reactions of 5–8 mg of TAB in cyclohexene were carried out with the Hanovia lamp for 5, 16, and 23 h. After five hours photolysis, the appearance is observed of the new maxima at 416 and 438 nm. Photolysis was continued until both these new maxima and the TAB CT maximum had largely disappeared: absorbance values less than 0.1. We note that the new absorbance maxima in sample aliquots will disappear over the course of several hours even without irradiation of the solution. Solvent volumes of photolyzed solutions were reduced to 5–10 ml by distillation under nitrogen, and spotted directly onto a LDI plate. Spotted samples were not protected from exposure to the atmosphere.

Trimesitylborane and tri-(2,6-dimethylphenyl)borane in cyclohexane solutions in Pyrex flasks were purged with nitrogen and then photolyzed under nitrogen for 23 h in front of the Hanovia lamp.

2.2. Materials

The triarylboranes, tri-(9-anthryl)borane, trimesitylborane, and tri-(2,6-dimethylphenyl)borane were synthesized by standard methods previously reported [20]. Carbon 13 NMR spectra (67.93 MHz) of tri-9-anthrylborane in deuteriochloroform were run in the laboratory of Florida State University by Tom Gedris. Both broadband and off resonance decoupled spectra were obtained. The spectrum is reported as chemical shift ppm down field, number of H on C, ring number assignment: 147.88, C (very weak), 9; 134.58, C, 8a; 131.40, C, 4a; 131.17, CH, 10; 129.28, CH, 1; 128.49, CH, 2; 126.07, CH, 4; 124.86, CH, 3. The assignment at carbon 10 is unambiguous as the intensity is roughly half that of other CH resonances.

2.3. Laser desorption ionization mass spectrometry

The LDI mass spectrometer was an Applied Biosystems Voyager DE sSTR (Framingham, MA). We operated the instrument in reflectron mode for all experiments and used anthracene, m/z 178.0777 and 9,9'-dianthryl product, m/z 354.1403, as internal standards for calibration. Experimental masses are all within 0.01 u of the assigned empirical formulas. This instrument uses a nitrogen laser at 337 nm and the laser power was changed in the typical way by rotating a neutral density wheel with computer control. The instrument control and acquisition software version was Voyager version 5.1 with Data Explore, Rev. A.

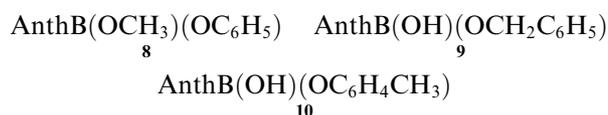
Sample preparation of arylboranes was done by dissolving the analyte of interest in toluene followed by spotting 1 μ L directly onto the LDI stainless steel plate. No additional chromophore containing molecule or acid was added to the sample. The LDI is expected to be a multi-photon process to achieve the necessary energy for ionization. The threshold of ionization was defined as the point at which a spectrum was observed with a signal-to-noise level of 10.

3. Results and discussions

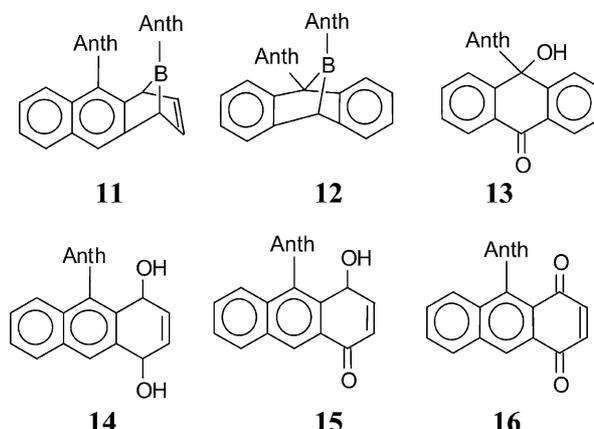
3.1. Solutions

Here, we report the results of a LDI MS analysis of tri-9-anthrylborane photolysis in toluene, cyclohexene, and tetrahydrofuran solutions. We expect predominately products from air autooxidation and hydrolysis of the initial organo-boron products. Products containing oxygen are important because they identify fragments originally bonded to boron. The oxidation of organo-boranes by molecular oxygen proceeds by a free radical mechanism through peroxide intermediates [21] such as RBOR(OOR) to yield boronic acid esters of the general formula RB(OR)₂, where R equals alkyl, or aryl. These molecules may then readily hydrolyze to alcohols and boronic acids. Interpretation of the data is aided by the natural isotope abundance of ¹⁰B and ¹¹B at 19.9% and 80.1%, respectively.

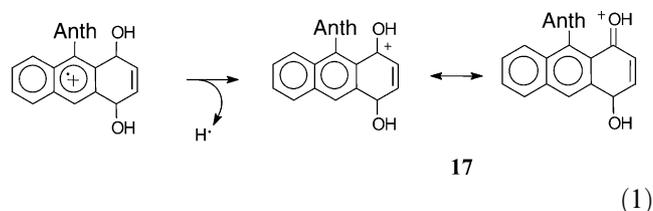
The LDI mass spectrum of photolysis products of TAB in toluene showed masses containing boron at *m/z* 312 (C₂₁H₁₇BO₂), and *m/z* 222 (C₁₄H₉B(OH)₂) in addition to the predominant mass peak at *m/z* 354 (C₁₄H₉-C₁₄H₉). The mass of 312 can be assigned to any or all of the compounds **8** through **10** below, derivable from borylene insertion into C–H or C–C bonds.



The mass spectra of the photolysis products of TAB in toluene also contain a significant series whose masses and assigned formulas are: *m/z* 388, C₂₈H₁₈(OH)₂; *m/z* 387, C₂₈H₁₇(OH)₂; *m/z* 386, C₂₈H₁₇O(OH); *m/z* 385, C₂₈H₁₆O(OH); and *m/z* 384, C₂₈H₁₆O₂. Isomeric structures of reasonable representative initial product boranes, **11** and **12**, and their oxidation products, **13** to **16**, are indicated below. The boranes **11** and **12** could be products either of AnthB: geminate recombination with 9,9'-dianthryl, or a photochemical rearrangement of TAB.



As illustrated in Eq. (1) for the radical cation of **14**, loss of hydrogen from ions of **14** or **15** yields a stable carbocation, **17**



Masses can also be assigned to AnthOH, *m/z* 194, and Anth-Anth-OH, *m/z* 370. The appearance of *m/z* 530 for dianthrylanthracene, Anth-Anth-Anth, is significant, suggesting rearrangement of an Anth-Anth-B(X)Anth species where X is H, OH, or alkyl by the same mechanism which produces dianthryl.

The LDI mass spectrum of the five-hour photolysis products of TAB in cyclohexene contained mass 318 (C₂₀H₁₉BO₃) in 10% abundance relative to dianthryl

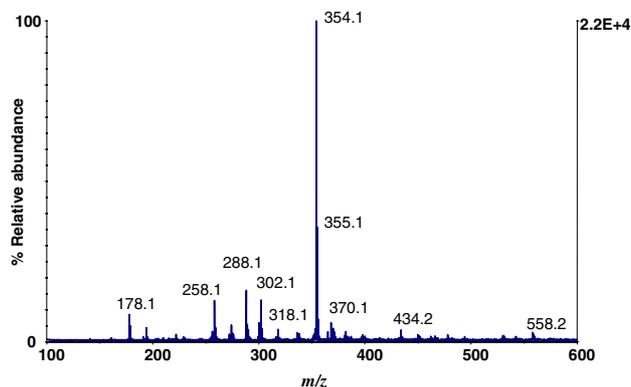
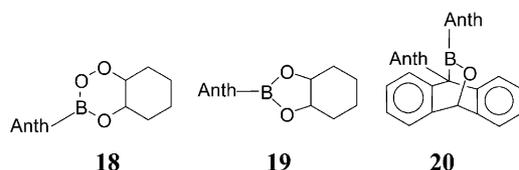


Fig. 1. LDI TOF MS of the photolysis products of TAB, *m/z* 542, in cyclohexene after 16 h. Product ions are observed at: *m/z* 558, C₄₂H₂₇BO; *m/z* 302, C₂₀H₁₉BO₂; *m/z* 318, C₂₀H₁₀BO₃; *m/z* 288, C₂₀H₁₆O₂ and *m/z* 258, C₂₀H₁₈ a cyclohexenyl-anthracene. Calibration masses are observed for anthracene at *m/z* 178 and dianthryl, the base peak at *m/z* 354.

and the most abundant mass was 542 from TAB. A photolysis reaction run for 16 h under the same conditions, resulted in the mass spectrum shown in Fig. 1. Because arylboronic acids and their esters (ArB(OR)_2 , where $\text{R} = \text{H, Alkyl, Aryl}$) are not oxidized by molecular oxygen under normal conditions, we assigned the origin of m/z 318 ($\text{C}_{20}\text{H}_{19}\text{BO}_3$) to structure **18** rather than AnthOB(OR)_2 . Structure **18** is also in keeping with the free radical mechanism proposed for the oxidation of alkylboranes by molecular oxygen. The mass at m/z 302 ($\text{C}_{20}\text{H}_{19}\text{BO}_2$) is assigned to structure **19**.

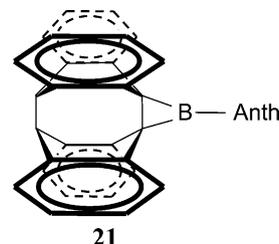


Given the extraordinary resistance of TAB to oxidation by molecular oxygen, assigning the mass 558 ($\text{C}_{42}\text{H}_{27}\text{BO}$) to $\text{Anth}_2\text{BOAnth}$ does not seem reasonable. We therefore prefer a structure such as **20** derived from oxidation of the result of AnthB: insertion into 9,9'-dianthryl or equivalent photochemical rearrangement. Although we do not see any product corresponding to that of **6** or **7** from AnthB: addition to cyclohexene, a related intramolecular mechanism beginning with boron carbon cleavage in the initial boracyclopropane product can account for the appearance of m/z 258 ($\text{C}_{20}\text{H}_{18}$), a cyclohexenyl-anthracene, and m/z 288 ($\text{C}_{20}\text{H}_{16}\text{O}_2$). As in the solvent toluene, masses are observed in low abundance for Anth-AntH-OH , AnthOH , anthracene, and dianthrylanthacene (Anth-AntH-AntH). These results in cyclohexene are in agreement with the reported isolation utilizing gas chromatography of aqueous solutions by Ramsey and Anjo [1] of 1,2-*cis*-cyclohexanediol from the Brown [21] hydrogen peroxide work up of cyclohexene solutions of tri-1-naphthylboron (TNB), photolyzed in soft glass ampoules. The later inability of Calhoun and Schuster [2] to find the reported *cis*-cyclohexanediol product, by extraction from water may be accounted for by the absence of the addition of mannitol required to free the glycol [22].

Photolysis of 5 mg of TAB in THF was carried out for three days under the GE Grow Light, after which time the 474 nm CT band of TAB was reduced to a shoulder on the side of a new maximum at 436 nm. LDI mass spectra of the products contain m/z 292, a result of borylene insertion followed by oxidation, [$\text{AnthB} + \text{THF} + 2\text{O}$], small amounts of 558, **20**, and the mass 222 of anthrylboronic acid (AnthB(OH)_2). As in other solvents, except for the base peak of dianthryl at m/z 354, product masses are all less than 20% relative abundance. Anthracene itself is a more abundant product in THF than in other solvents. Differences between

results in THF and other solvents may be the result of the ability THF to coordinate strongly with organoborane intermediates and boron containing products. These results are in agreement with those of Pachaly and West for the reaction of $(\text{C}_6\text{H}_5)_3\text{SiB:}$ with THF, where insertion of the borylene into the THF ring was observed [23].

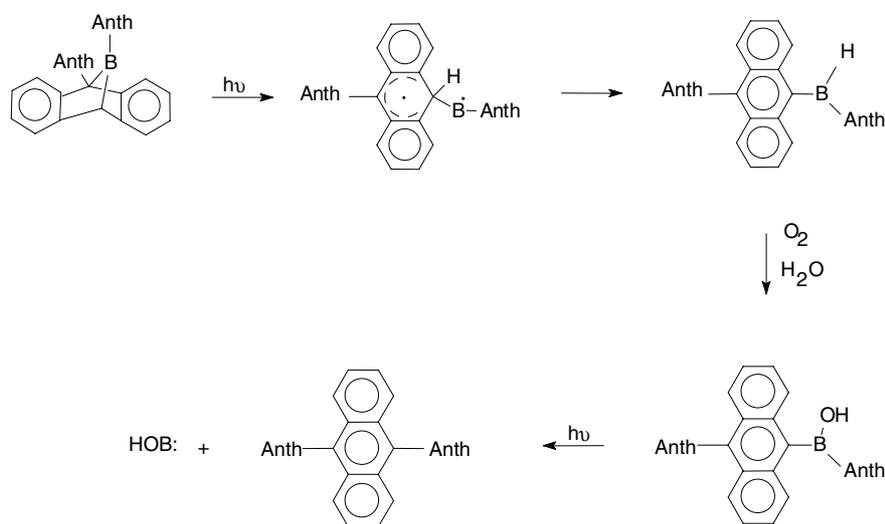
The observed results of the solution photolysis of TAB in toluene, THF, and cyclohexene, suggest that the principal photolysis pathway of TAB proceeds with the formation of an intermediate characterized by the appearance of the new UV maxima. Known photochemical reaction mechanisms such as that of anthracene photodimerization [24] or the di- π -methane rearrangement [25] combined with allowed 1,3 or 1,5 sigmatropic rearrangements could produce any of the intermediate molecules, **11**, **12**, and/or **21**, the internal photodimerization product of TAB. This intermediate then, either thermally or photochemically, yields 9,9'-dianthryl and anthrylborylene (AnthB:) within a solvent cage. Geminate recombination offers an alternative path to **11** or **12** and the products in toluene (masses 388 to 384), and **20**, m/z 558, in cyclohexene. Borylene reactions with solvent produce the previously discussed products. Borylene trapping by cyclohexene is faster than by toluene.



Each of the structures **11**, **12**, and **21** also possess a chromophoric unit, AnthBR_2 , which would be expected to exhibit a UV maximum to the blue of the TAB maximum, accounting for the appearance of the new maxima at 416 and 438 nm during photolysis in cyclohexene and 436 nm in THF.

Ring opening at a boron-carbon bond of either intermediate **12**, or **21**, and subsequent reactions with solvent or traces of water would also produce the necessary precursors to the trianthryl and hydroxydianthryl, observed among the photolysis products of TAB in toluene and cyclohexene as shown in Scheme 1.

As in the photolysis of tri-1-naphthylboron, there is a free radical component to the solution photochemistry of TAB. In small abundance, mass numbers are observed for products of the addition of solvent radicals to dinaphthyl where the solvent is: toluene, m/z 444; cyclohexene, m/z 434; THF, m/z 424, and addition to anthracene in THF, m/z 258. The neutral solvent radicals are



Scheme 1.

the products of hydrogen abstraction by either triplet borylene, or dianthrylboryl and anthryl radicals.

In common with TAB, the intense charge transfer maxima of TXYB (316.8 nm) and TMB (331.3 nm) in hexane disappear on irradiation from the Hanovia UV source through a Pyrex® filter. There is no evidence of 1,3,5-trimethylbenzene (mesitylene) or 1,3-dimethylbenzene (*m*-xylene) in the UV spectra of photolyzed solutions. Instead the spectra are characteristic of the hindered biphenyls rather than substituted benzenes [26]. The spectra exhibit intense rising end absorption from 300 to 210 nm with one to two inflection points between 230 and 300 nm.

3.2. Mass spectrometry of triarylborylene solids

These observations in solution led us to compare the laser desorption mass spectra of TXYB and TMB with that of TAB to search for evidence of photochemistry before ionization. We obtained the LDI spectra of the three triarylborylenes over a range of laser powers, varying from 2% and 5% above the threshold power, to power levels 30% to 50% above the threshold level where extensive ion fragmentation was observed. For comparison purposes, the LDI spectra of anthracene and 5-methylchrysene were obtained over a similar laser power range. The vertical ionization energy [27] of anthracene is 7.40 eV. The laser photon energy of 3.68 eV (356 kJ/mol) makes an efficient soft two photon ionization process possible in which ionization occurs out of a vibrationally excited first electronic excited state of anthracene. At a laser power 10% above threshold in our LDI-MS, the masses 178 (100%), 179 and 180 of anthracene, and 376 (4%) are the only masses observed in greater than one percent abundance in the range 50–500 u. For the later purposes of discussion of the LDI spectra of TAB, the important observation

is the absence of *m/z* 177 from the loss of hydrogen. At a laser power of 20% above threshold, *m/z* 177 and other ions of lower mass begin to appear in the spectrum of anthracene. The ion of *m/z* 376 reaches 25% abundance.

The ionization energy of TAB is identified, through Koopmans' theorem [28], with the energy of the highest occupied π orbital of TAB, which will be largely localized on the three anthracene rings. The energy of this orbital is determined by the competing electron releasing inductive effect of boron, which would raise the orbital energy, and mixing of the vacant boron 2p function into the anthracene highest occupied π orbital, which would lower the orbital energy, increasing the ionization energy. Assuming sp^2 hybridization of the boron, mixing of the vacant boron 2p orbital into the anthracene π orbitals is limited by both the energy gap between the functions and the fact that for steric reasons the anthracene rings are rotated well out of the plane of the boron to carbon bonds reducing the overlap of the vacant boron 2p with the anthracene π orbital. The C13 NMR chemical shifts of the 1 (129.3 ppm), 3 (124.9 ppm), 4 (126.1 ppm), and 10 (131.2 ppm) carbons of TAB are all up field with respect to the corresponding C13 shifts in anthracene, 130.1, 125.4, 130.1 and 132.6 ppm. The chemical shift of carbon 2 (128.5 ppm) in TAB is downfield from that of anthracene at 125.4 ppm. If we utilize the relative chemical shifts of the number 4 and 10 carbons as a measure of change in π electron density, we conclude that in the case of TAB, the boron vacant 2p does not significantly interact with the π HOMO of anthracene, and that the ionization potential of TAB should be close to and probably less than that of anthracene. A soft two photon ionization should therefore be possible in TAB.

Two mass spectra of TAB are shown at two different laser intensities of 2100 and 2500 in Fig. 2(a) and (b),

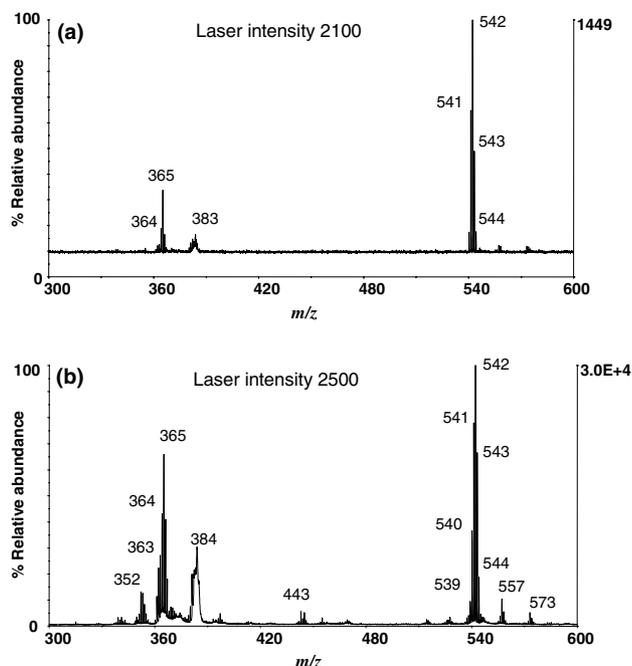


Fig. 2. LDI TOF MS of tri-9-anthrylborane (TAB) at (a) low, 2100 and (b) high, 2500, laser power. At the higher power, increased overall signal is observed with increased relative abundance of the fragments. Loss of at least one hydrogen atom accounts for the change in ion ratios observed at the distribution at m/z 365 and m/z 542. Metastable ion production is observed by the broad peak at m/z 384.

respectively. The threshold laser intensity, 2000 in our experiments, for ionization of TAB is found to be the same as that for anthracene. Mass spectra with $S/N > 10$ are obtained at laser intensities 5% above this at 2100. In the representative mass spectrum in Fig. 2(a), the following products were observed with indicated chemical formula and mass: anthracene, $C_{14}H_{10}$, 178 (not shown); $C_{28}H_{17}B$, 364; $C_{28}H_{18}B$, 365; $C_{28}H_{15}B_3$, 384; $C_{42}H_{26}B$, 541; $C_{42}H_{27}B$, TAB, 542; $C_{70}H_{43}B_2$, 905 (not shown). The overlapping mass spectral peaks of the parent ion of TAB, 542, and TAB after loss of one hydrogen, 541, were analyzed by fitting the observed peaks between 540 and 544 to the sum of theoretical spectra for TAB and [TAB-H] in varying ratios. Between a laser intensity range 2000–2200, the calculated ratio of TAB/[TAB-H] ion abundance was typically about two. The relative abundances of m/z 541 and 542 can also be fit by a single species $C_{27}H_{19}B_2$. This would require some mechanism in which a carbon is lost from one of the anthracene rings, perhaps as the result of borylene insertion into an anthracene ring. The mass peaks in the spectrum of TAB at m/z 365 and 364 at low laser intensities equate to a four to one mixture of $C_{28}H_{18}B$ and $C_{28}H_{17}B$. This interpretation would be consistent with the simple loss of one anthracene from the TAB ions of mass 542 and 541 to form (Anth)₂B. The structure of Anth-AnthBH is an isomeric alternative whose origin would be a photochemical product such as **12**.

The ready cleavage of hydrogen from anthracene rings in the LDI ionization of TAB requires a facilitating mechanism. One possible mechanism would certainly be photochemical generation of AnthB: which then inserts into a C–H bond of TAB. This would be followed by loss of AnthBH with the net result of removing one hydrogen from TAB. At a laser intensity of 2500, m/z 189 at 5% relative abundance (not shown) and its corresponding isotopic peaks were identified as $C_{14}H_{10}B$, AnthBH. The peak near m/z 384 in the LDI ionization of TAB (especially in Fig. 2(b)) appears to be that of a metastable ion, as it is broad and unresolved from m/z 382 to 385. The empirical formula $C_{28}H_{15}B_3$ is suggested because this keeps the anthracene rings intact and is consistent with borylene additions to the anthracenyl rings of TAB. In keeping with the postulate that the ion of Anth₂B results from photon induced fragmentation of the parent ion, Anth₃B, the abundance of mass 365 increases to 70% with an increase in laser intensity from 2000 to 2500 as shown in Fig. 2(b). This is not the pattern observed for TXyB or TMB.

The ion at m/z 905 (not shown in Fig. 2(b)) reaches an abundance of 20% at a laser intensity of 2500, and is identified as a product of the addition of either Anth-AnthBH to TAB with subsequent loss of one hydrogen each from boron and an anthryl ring, or C–H insertion of Anth-AnthB: into TAB with loss of H from boron. The latter explanation finds support in the appearance in the spectrum of masses at 352, 353, and 354 derivable from dianthryl radical (Anth-Anth-). Addition of Anth₂B, radical or ion, to TAB requires a subsequent loss of not one, but two hydrogens from anthryl rings to reach a m/z 905, which seems less likely.

The LDI mass spectrum of TXyB, $C_{24}H_{27}B$, at a laser intensity 2200, just above threshold, is shown in Fig. 3(a). We make the following formula and mass assignments: $C_{15}H_{14}B$, 205; $C_{16}H_{17}B$, 220; $C_{16}H_{18}B$, 221; $C_{23}H_{24}B$, 311; $C_{24}H_{26}B$, 325; $C_{24}H_{27}B$, 326. The abundance ratio of $C_{24}H_{27}B$, m/z 326 to $C_{24}H_{26}B$, m/z 325 was calculated to be 2.5 in a typical mass spectrum. With an increase in laser intensity to 2700, abundances increase sharply as shown in Fig. 3(b) and new masses appear at $C_9H_{12}B$, 131(7) and $C_{32}H_{35}B_2$, 441 (5) (not shown in Fig. 3(b)).

The appearance of the Ar_2B^+ ions of TXyB and TMB in much greater abundance than the Ar_3B^+ precursor ion at m/z 326, at low laser intensity and the subsequent increased relative abundance of the precursor ion as compared to Ar_2B^+ with increasing photon intensity is unexpected as it is the opposite of the effect observed with TAB. This difference in the cases of TXyB and TMB is attributed to initial photochemical fragmentation of neutral Ar_3B in its lowest excited state to Ar_2B and Ar neutral radicals, followed by ionization of the Ar_2B radical. Ionization of TXyB and TMB are necessarily an inefficient three photon process which occurs

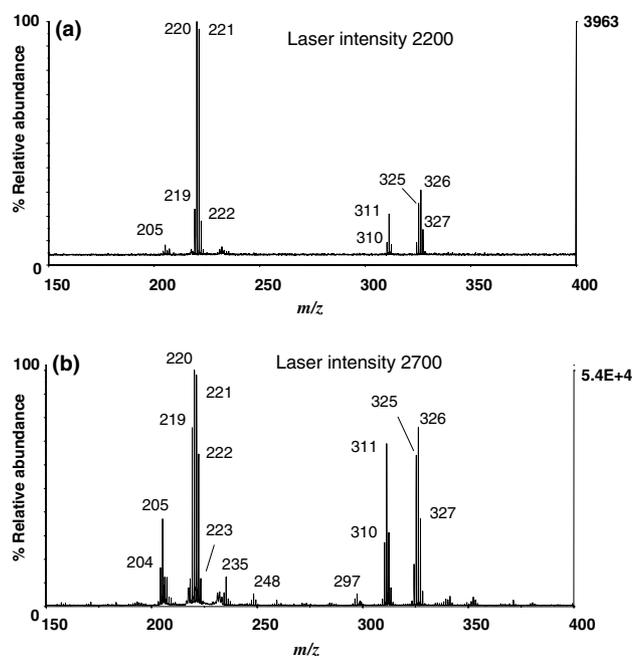


Fig. 3. LDI TOF MS of tri-(2,6-dimethylphenyl)borane (TXyB) at (a) low, 2200 and (b) high, 2700, laser power. At the higher power, the overall signal and fragmentation is increased, but with the unexpected increase in the relative abundance of Ar_3B^+ at m/z 326. This relative increase in the precursor ion over the fragmentation products is explained by the improved ionization efficiency of the parent at higher laser powers. The loss of at least one hydrogen atom accounts for the change in ion ratios observed at the distribution at m/z 220. The onset of metastable ion production is observed by the broad peak at m/z 232.

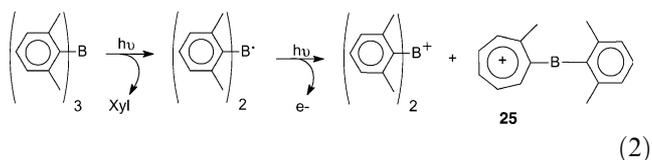
from a molecular Rydberg, rather than lowest excited, state of the molecule. With increasing laser intensity, ionization of Ar_3B becomes more competitive with this fragmentation (see Fig. 3(a) and (b)).

Since the loss of methyl, mass 15, from the parent TXyB, 326, to give the ion of mass 311 was unexpected, the LDI spectrum of 5-methylchrysene was measured as a convenient model. At a threshold laser power of 2600, the m/z (% relative abundance) observed are 241 (12), 242 (100), 248 (8), and 255(10). Increasing the laser intensity to 2800 produces the appearance of additional

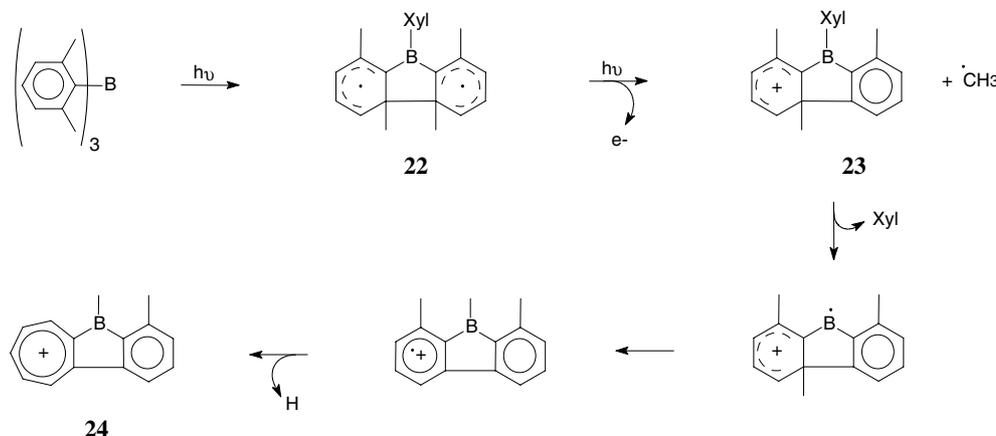
ions at masses 240 and 239, but not 237. At a laser intensity of 3000, mass 239 (70) is the second most abundant ion present and mass 237 has an abundance of 15%. We conclude, therefore, that the loss of a methyl group from the benzene rings of TXyB requires some mechanism other than simple fragmentation from an excited state of TXyB or its ion.

The presence, although in low abundance, of XyBCH_3 (131) in the mass spectra, suggest XyB : insertion into a methyl to carbon bond of TXyB in a melt or solid phase photochemical reaction followed by loss of XyBCH_3 . The steric requirements, however, around the *ortho* positions of TXyB are unfavorable. Alternatively, we suggest a mechanism such as photochemical coupling across the 2,2' positions of the benzene rings of TXyB to yield **22**, photoionization with loss of methyl to form **23** (mass 311), loss of xylyl, 1,3 sigmatropic migration of methyl to boron, and finally loss of hydrogen from methyl with ring expansion to **24** (mass 205), containing the aromatic tropylium ring, (Scheme 2). The methyl migration is symmetry allowed suprafacial if photochemical, and antarafacial or suprafacial with inversion if from a ground state.

Ionization of the neutral dixylylboryl radical Xy_2B , a product of photochemical cleavage of TXyB, readily accounts for the appearance of mass 221 among the products. The appearance of mass 220 as the most abundant ion in the spectrum again, however, suggest an energetically favorable loss of hydrogen to form the ion **25** containing the aromatic tropylium ion structure, Eq. (2)



The low abundance of masses in the LDI mass spectrum of TXyB at 441 and 546 can be regarded as addition products of XyB : or $(\text{Xy})_2\text{B}$ to TXyB, respectively, followed by the loss of one hydrogen, either from boron



Scheme 2.

or the benzene ring. Alternatively, the loss of one xylil from the ions of mass 546 produces an ion of mass 441. We ran an LDI mass spectrum on a mixture of TXYB and TAB, and observed cross product ions of mass 763 (XY₂B-TAB) and 689 (Anth₂B-TXYB). These bimolecular reactions may be taking place in a melt prior to vaporization rather than in the gas phase.

The additional presence of a methyl group in the 4, 4' and 4'' positions of TMB leaves the LDI mass spectrum of TMB unchanged with respect to that of TXYB, in that ion masses observed for TMB have a one to one correspondence to those of TXYB except for an addition of 14 u.

4. Conclusions

LDI mass spectrometry serves as a useful method for the selective analysis of products from a complex reaction mixture of the photolysis products of tri-9-anthrylborane. LDI mass spectrometry also proves to be a unique and convenient method for obtaining arylborane mass spectra with prominent molecular ion peaks for the purposes of molecular weight and structure determination.

Photolysis of tri-9-anthrylborane (TAB), in solvents cyclohexene, toluene, and tetrahydrofuran, produces 9,9'-dianthryl and 9-anthrylborylene which then undergoes addition or insertion reactions with solvent molecules. The products are similar to, but not always identical with, products reported in other "borylene" reactions. In the formation of dianthryl and other biaryls during photolysis, new bond formation occurs across the 1 to 1' aryl carbons. Photochemical arylborylene formation from TAB or TNB could occur by a simple concerted symmetry allowed one step process yielding diaryl and arylborylene. Alternatively, species such as 9-anthryl-9',10'-(9''-anthrylborenyl) anthracene, **12**, or the product of internal anthracene photodimerization, **21**, are the intermediate precursors to the formation of 9,9'-dianthryl and anthrylborylene. These and previous results suggest that this method of borylene formation could be extended to molecules of the general structure Anth₂BX, where X is alkyl, OH, OR, halogen or NR₂, and in matrices where spectroscopic characterization of the organo-borylenes would finally be possible.

Soft two photon resonance ionization of TAB yields the ground state parent molecular ion, Anth₃B⁺, which on excitation by additional photons, fragments to the di-9-anthrylboryl ion (Anth₂B⁺) and anthryl radical (C₁₄H₉). The appearance of ions of mass one less than that of parent TAB and Anth₂B⁺ are best explained as LDI ionization of products resulting from the insertion by AnthB: into a C–H bond of TAB. This reaction seems more likely in a liquid melt or solid phase prior to ionization than the gas phase. Fragmentation of Ant-

hBH-C₁₄H₈-BAnth₂ would then carry away one hydrogen from TAB.

Ionizations of trimesitylborane, TMB, and tri-(2,6-dimethylphenyl)borane, TXYB, occur by a three photon process out of high lying molecular Rydberg states. This necessarily inefficient process must compete with photochemical fragmentation of the first electronic excited states of neutral TXYB and TMB into aryl and diarylboryl radicals, which then undergo subsequent photoionization to (Aryl)₂B⁺ ions. Ions exhibiting loss of methyl groups are attributed to rearomatization, by methyl loss, after ortho photochemical cross coupling of benzene rings in neutral TXYB and TMB. The appearance in low abundance of *m/z* 131 in spectra of TXYB and *m/z* 145 in TMB spectra, corresponding to ArylBMe offer an alternative borylene insertion mechanism for methyl loss. A large abundance of ions with masses one less than a parent ion is attributed to facile loss of hydrogen from methyl followed by ring expansion to an aromatic tropylium ion structure.

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