Computational Chemistry as a Conceptual Game Changer: Understanding the Role of London Dispersion in Hexaphenylethane Derivatives (Gomberg Systems)

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Abstract: The present personal perspective sheds light on the checkered history of hexaphenylethane (HPE) and some of its key derivatives, including successes and failures in interpreting experimental as well as computational data. HPE has become a testing ground for chemical theory since the groundbreaking work of Gomberg in 1900. It sparked the growth of theoretical carbon chemistry beyond tetravalency, forced chemists to improve theory of color and chemical bonding by mesomeric resonance, and challenged the purely repulsive view on substituent effects. Understanding the origin of the instability of HPE on the one hand and the stability of the sterically much more crowded all-meta ^{t}Bu-substituted HPE on the other hand may well be considered an important turning point in the appreciation of London dispersion (LD) and the analytical power of computational chemistry.

Keywords: Bond Lengths · Hydrocarbons · Noncovalent Interactions · London Dispersion · Radicals

Hexaphenylethane: What a Story!

Gomberg arguably is the godfather of organic radical chemistry and the discoverer of the trivalent carbon.[1] As a very skilled and meticulous chemist,[2] he was vexed by his initial failure to synthesize hexaphenylethane (HPE) and arrived at the conclusion that this is due to HPE being a very reactive *unsaturated* hydrocarbon. In a scientific world in which the concept of free radicals was thought to be a mere "speculative invention" and deviation from Kekulé's axiom of the tetravalent carbon equaled heresy,[3] Gomberg trusted his analyses and bravely concluded that *"Die [...] mitgetheilten experimentellen Ergebnisse zwingen mich zu der Annahme, dass in dem 'ungesättigten Kohlenwasserstoff' das Radical Triphenylmethyl vorliegt"* (the experimental findings force me to assume that the "unsaturated hydrocarbon" presents the triphenylmethyl radical).[1a] From thereon, a fervid debate about the structure and properties of "triphenylmethyl", its dimers and derivatives began, which is still vital and ongoing more than 120 years later.

The Years Before 1900

Lavoisier first mentioned the term "radical" in 1789 as the oxidized element in an oxygen acid.[4] In the following years until 1840, it was unpopular to call an element a radical. Still, the term persevered as a description accounting for repeating units in sum formulas, e.g., the etherin radical "C_4H_4"[5] was present in ethanol "C_4H_4,H_2O" or ethyl acetate "$C_4H_4,C_2H_4O_2$".[3] Kekulé summarized radicals appropriately as: *"Nach unserer Ansicht sind Radicale nichts weiter als die bei einer bestimmten Zersetzung gerade unangegriffen bleibenden Reste"* (In our opinion, radicals are simply unchanged residues during decompositions).[6] Free radicals like methyl "C_2H_3" were assumed, but proven to be dimers, here, ethane „C_4H_6".[3] In 1858, Kekulé recognized and postulated the principal tetravalency of carbon.[7] This view hardened in the chemical community and deviation from it was often dismissed *per se* without further consideration.[3] Even though the radical notion as stated by Kekulé remained, it was increasingly faced with doubt.

During this time, Gomberg obtained his chemical education. After escaping from Russia, he arrived in the USA and worked hard to pursue his education. He enrolled in the University of Michigan in 1886, obtained his PhD in 1894, and gained a solid background in analytical and organic chemistry.[2] In 1896/97, Gomberg conducted research in Munich with Adolf von Baeyer and in Heidelberg with Victor Meyer, where he synthesized the long elusive tetraphenylmethane.[8] Lacking modern spectroscopic tools, structural elucidations were based solely on elemental analy-

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sis, changes in melting (cryoscopy) or boiling points (ebullioscopy) of mixtures as well as chemical behavior. One of Gomberg's main structural proofs for tetraphenylmethane was the lack of color upon treatment of the tetranitro derivative with aqueous KOH.[9] Back in Michigan, Gomberg envisioned the synthesis of the next higher homologue in the series of perphenylated alkanes –HPE (H-1_2)– to repeat this structural proof, ensure its validity, and back up the success of his former synthesis of tetraphenylmethane.

Gomberg and the First Organic Radical

In 1900, Gomberg published his *"Triphenylmethyl, ein Fall von dreiwertigem Kohlenstoff"* in the famous *Berichte der Deutschen Chemischen Gesellschaft*,[1a] thereby also describing his attempts to synthesize H-1_2. Wurtz coupling of triphenylmethyl bromide and chloride with sodium in benzene proved unsuccessful. The same reaction with silver, mercury or zinc yielded an insoluble, crystalline solid which he found to be the peroxide after meticulous examination *via* elemental analysis and comparison to an authentic reference compound. Molecular weights were accessible neither by cryoscopy due to poor solubility, nor by ebullioscopy due to the temperature sensitivity of the compound. Exclusion of oxygen by conducting the reaction with freshly reduced silver (or better, zinc) in a CO_2 atmosphere yielded a solid hydrocarbon that was readily soluble in benzene and stable over weeks in the absence of oxygen. This hydrocarbon behaved as if highly unsaturated because it reacted *"mit größter Begierde"* (with eagerness) with O_2, Cl_2, Br_2 and even with diluted solutions of I_2 to give the corresponding peroxide, chloride, bromide, or iodide, respectively. Gomberg therefore concluded that the unsaturated hydrocarbon corresponds to the triphenylmethyl radical (H-**1**, Figure 1).

The possibility of the formation of H-1_2 (=HPE) was dismissed because different chemical behavior would be expected of a perphenylated hydrocarbon. Gomberg also vouched for a new type of trivalent carbon, unlike that found in unsaturated systems. This unsaturated trivalency might arise from the impossibility to add a second, *"zu viel des Raumes […] beanspruchenden"* (bulky) triphenylmethyl group to form H-1_2. Note that literally the same paper was published (just translated) in the *Journal of the American Chemical Society* soon thereafter.[1b] This was not only acceptable but even customary at the time, as was the claim at the end of the paper "*This work will be continued and I wish to reserve the field for myself*".

The Early "Triphenylmethyl" Period

These findings were soon challenged by Norris and Sanders,[10] by Markovnikoff,[11] and later by Ullmann and Borsum.[12] Norris and Sanders first argued against the originality of Gomberg's publication as they also had synthesized the same hydrocarbon previously.[13] A second provocative paper named "On The Non-Existence of Trivalent Carbon" discarded Gomberg's idea of a trivalent carbon by postulating a quinoid structure of a monomeric "triphenylmethyl" (TMP)[14] – a structural element that was of high importance for the next 15 years of vital discussions. Gomberg defended the originality of his work[15] and answered the second Norris/Sanders publication thoroughly by disproving it point by point.[16] Another disturbance was introduced as Ullmann and Borsum claimed to have synthesized HPE.[12] Gomberg found the same

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$$(C_6H_5)_3 C.$$

Figure 1. Gomberg's first visualization of the triphenylmethyl radical. Reprinted with from ref.[1a] Copyright (2021) John Wiley and Sons.

$$(C_6H_5)_3 CCl \overset{Zn.Cl}{\underset{Cl}{<}}$$

Figure 3. Gomberg's representation of the zinc(II)chloride salt of trityl chloride. Reprinted from ref.[22] Copyright (2021) John Wiley and Sons.

stable hydrocarbon after treatment of "triphenylmethyl" with acids and also concluded that this was HPE.[17] Not until two years later, in 1904, Tschitschibabin brominated this hydrocarbon and hydrolyzed it to the corresponding alcohol. This alcohol only could arise from *para*-benzhydryltetraphenylethane and therefore disproved the HPE claim.[18]

A substantial debate about the structure of "triphenylmethyl" arose and until 1905, when all structures considered relevant from today's viewpoint were already postulated, namely monomeric triphenylmethyl (H-**1**)[1] and its quinoid mesomer (H-**1'**),[10] -note that the concept of resonance had not been established at the time- as well as the dimers hexaphenylethane (H-**1**₂/HPE),[11] a singly (**2**)[19] and a doubly (**3**)[20] quinoid isomer (Figure 2).
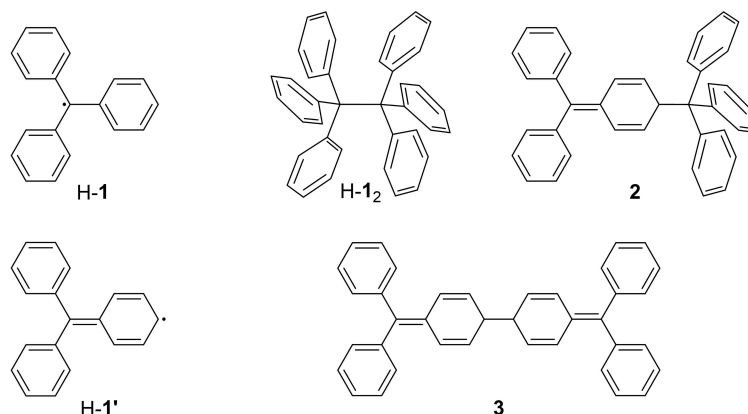
The Quinoid structures. Quinoid structures were initially proposed to account for reactivity and color. The yellow color was first mentioned by Norris and Sanders in 1901.[10] They attributed the reactivity and especially the color to the quinoid substructure in the "tautomer" H-**1'**. This view was also held by Kehrmann and Wentzel.[21] Gomberg argued against this view, gave colorless examples of such quinoid structures and had even obtained the solid "triphenylmethyl" as colorless crystals.[16] Only the connection between the colored solutions and the quinoid structure remained a point of discussion for him. By 1902, it had become evident that "triphenylmethyl" had two modifications. Gomberg could now show that solid "triphenylmethyl" was indeed colorless, while solutions were always yellow.[22] Gomberg switched from the opposing Kehrmann-Wentzel/Norris-Sanders theory to Baeyer's recent theory of halochroism and attributed the color to a heterolysis of "triphenylmethyl" into "pseudoions". This agreed with the appearance of the same color upon treatment of trityl chloride
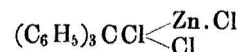
with ZnCl₂, to which the following structure was attributed (Figure 3): Shortly thereafter, Gomberg re-advertised the TPM idea based on the isolation of trityl iodide.[23] While the reaction of iodine with "triphenylmethyl" was already found two years earlier, the isolation was impeded by its similar reactivity in solution towards oxygen akin to "triphenylmethyl". Gomberg keenly recognized that *"in ungesättigten Verbindungen zwei Affinitäten unter Bildung einer Doppelbindung verbraucht werden [und] wenn eine solche Verbindung unter gewissen Umstanden durch Halogene gesättigt wird [...] lagert sich [...] an [beide] Kohlenstoffatome ein Halogenatom an. Aber in dem hier beschriebenen Kohlenwasserstoff addirt sich alles Iod nur an ein einziges Kohlenstoffatom - und daraus muss geschlossen werden, dass der Zustand des Ungesättigtseins sich nur auf ein Kohlenstoffatom erstreckt. Von diesem Gesichtspunkte aus sollte daher dem Kohlenwasserstoff die Formel [H-1] zugeschrieben werden."* (two affinities are consumed for one double bond in unsaturated compounds and if such compounds are saturated with halogens, halogen atoms are added on both carbons. Instead, only one iodine atom is added in the described hydrocarbon – we therefore have to conclude that the state of unsaturation belongs only to one carbon atom. From this point of view the structure [H-**1**] shall be assumed for the investigated hydrocarbon).

In the meantime, the discussion about the molecular structure was enriched by Heintschel's double quinoid dimer structure **3**,[20] another instance of the quinoid mesomer to account for reactivity and color. Subsequently, the dimeric nature of "triphenylmethyl" received support in 1904 when

Figure 2. Suggested structures in the discussion on radicals and HPE (H-1₂): the monomeric triphenylmethyl radical (H-1), its quinoid mesomer (H-1'), and the dimers HPE, singly (2) and a doubly (3) quinoid isomers.
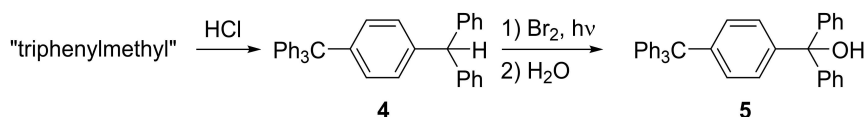
Figure 4. Ullmann's hydrocarbon **4** is obtained after treatment of "triphenylmethyl" with dry HCl.[12] Tschitschibabin subsequently obtained alcohol **5** *via* bromination and hydrolysis.[18] Jacobson took the acid catalyzed re-aromatization as evidence for **2**.[19]

(after initial problems with the cryogenic determination of the molecular weight of "triphenylmethyl")[24] Gomberg published a final molecular weight of 477, which is almost double the weight of the monomer (243).[25] This clearly pointed towards a dimeric structure. Hence, Gomberg gave up a solely monomeric "triphenylmethyl" and mentioned an equilibrium between an associated and dissociated "triphenylmethyl", which could not be **3**. Higher temperatures yielded a deeper color as well as a lower molecular mass. Both pieces of evidence pointed towards a temperature-dependent equilibrium of a colored and an uncolored form.

Based on Tschitschibabin's publication on the wrong "HPE",[18] Jacobson immediately suggested an unsymmetric dimer, namely 1-diphenylmethylen-4-triphenylmethyl-cyclohexa(2,5)diene **2**.[19] He based this structure on the acid catalyzed rearrangement of "triphenylmethyl" to Ullmann's hydrocarbon (Figure 4). This was the first solid evidence that could have led to the assignment of the correct structure. Yet, it was questioned.[26]

In 1905, Gomberg formulated his dilemma:[26d] On the one hand, Jacobson's structure **2** (the Jacobson-Nauta structure, JNS) accounts for a dimer, the rearrangement to Ullmann's hydrocarbon, and evades the postulation of a trivalent carbon. It does not explain the observed reactivity and color (now Gomberg invoked the lack of color of known quinoid structures). On the other hand, TPM explained its chemical behavior perfectly, but contradicted the experimental mass. A true equilibrium was not yet recognized and Gomberg instead made use of an alternative explanation by postulating an association of H-**1**, similar to the dimerization of carboxylic acids to account for the odd molecular weight.[26d]

Even more evidence towards a quinoid dimeric structure came in 1906 by Gomberg himself. In an attempt to solve the dimeric structure of "triphenylmethyl" experimentally, he treated *para*-halogenated triphenylmethyl chlorides with silver.[27] The amount of extracted chloride then should provide hints regarding the binding mode of the corresponding carbon (Figure 5) and therefore whether H-**1**$_2$, **2** or **3** was present; the results excluded H-**1**$_2$ but did not allow for a differentiation between **2** or **3**. Later results also excluded an *ortho*-quinoid structure.[28] In 1907, Gomberg concluded that "triphenylmethyl" mesomerizes in solution into **2** which is in equilibrium with H-**1**. *"[...] die Konstitution des in Lösung befindlichen Kohlenwasserstoffes [ist] schon jetzt als mit befriedigender Sicherheit aufgeklärt [als] Jacobson zugeschriebene Formel[...]"* (the constitution of the dissolved hydrocarbon is already characterized securely as Jacobson's suggested formula).[29]
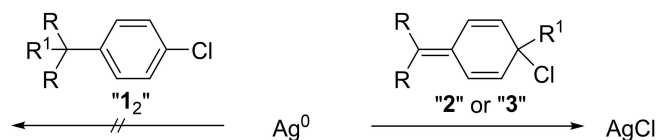
Figure 5. Abstraction of the *para*-chloride from a benzoic structure as in **1**$_2$ was thought to be difficult while the abstraction from the quinoid position was assumed to proceed readily. Today, this would be explained by the difference in radical stability between a phenyl radical localized in an sp^2-orbital and a stabilized allylic radical in a delocalized π-orbital.

The Hexaphenylethane (HPE) Structure. Another group preferred H-**1**$_2$ as the structure of "triphenylmethyl". Already in 1902, Markownikoff attributed the high reactivity of "triphenylmethyl" to a very unstable H-**1**$_2$.[11] Later, Flürscheim – an advocate for a "mesomeric resonance" – argued that this "resonance" might lead to the abnormal formation of Jacobson's hydrocarbon **2**.[26b] Nonetheless, the direct formation of a bond between the carbon atoms of the highest affinity and thus the formation of HPE seemed more likely. "Triphenylmethyl" therefore could be colorless H-**1**$_2$ in equilibrium with colored H-**1**. Tschitschibabin also preferred the HPE structure of "triphenylmethyl", but stated that one could not exclude Jacobson's structure, for the same reasons Jacobson had named.[26c] This was immediately challenged by Gomberg in 1905, who excluded HPE because of the presumably "saturated" character of this hydrocarbon, the impossibility to form similar, less phenylated ethanes at the time[26d] and, in 1906, due to the experimental *para*-halogen lability.[27] After tetra- and pentaphenylethane had been synthesized, Gomberg argued the opposite (but still against H-**1**$_2$): *"So dürfen wir doch aus der Existenz [...] des Tetraphenyl- und Pentaphenyl-Aethans, schliessen, dass auch Hexaphenyläthan existenzfahig ist, und dass es, einmal gebildet, sich als beständiger und wenig reactionsfähiger Kohlenwasserstoff erweisen wird."* (We have to conclude from the existence of tetra- and pentaphenylethane that HPE, once formed, will be a stable and inert hydrocarbon).[27]

The last chemical evidence (beside the acid catalyzed rearrangement and *para*-halogen lability) was noticed early in 1901, but only brought to completion 70 years later: A liquid autooxidation byproduct referred to as "the oil".[30] The yield of bis(trityl)peroxide upon quenching of a "triphenylmethyl" solution with oxygen was only about 80%, even though a full equivalent of oxygen was consumed. The remaining 20% contained mainly an oily oxidation byproduct of

"triphenylmethyl". This caught the attention of Gomberg, who reinvestigated "the oil",[24] and Norris, who stated that "*[the oil] has not received in the past the attention that it deserves.*"[31] Gomberg examined the oxidation of "triphenylmethyl" to the peroxide in detail and found increased amounts of "the oil" by usage of absolute oxygen instead of air. However, *"Wir haben diese öligen Producte übrigens keiner eingehenden Prüfung unterzogen und uns auf die Feststellung beschränkt, dass [die Öle] etwa ebensoviel Sauerstoff wie das Peroxyd selbst enthalten"* (We did not analyze "the oil" further and leave it with the notion that it contains as much oxygen as the peroxide).[25] Norris' opinion "*As an oil [is] at times present, an investigation of the cause of the formation of [this substance] must be made before the reaction,[32] which is evidently a very complex one, can be exactly interpreted*" would finally prove correct. Deeper insights were gained in the 1930s[33] and the problem was solved in the 1970s,[30a] as will be shown later.

By the end of 1907, Gomberg admitted, regarding the constitution of solid "triphenylmethyl": *"eine Auswahl zwischen [den Möglichkeiten[34]] zu treffen, [...] mehr Sache des persönlichen Gefühls als der logischen Deduktion"* (a distinction between the options is rather a matter of personal flavor than logical deduction).[29]

More light was shed on the "triphenylmethyl" puzzle, when Schmidlin observed a temporary decolorization of a "triphenylmethyl" solution if shortly exposed to oxygen.[35] This was rationalized by an equilibrium between an unreactive colorless and a reactive colored form in accordance with Gomberg's earlier hypothesis[25] of such an equilibrium. Subsequently, Flürscheim advertised his earlier view of an equilibrium between colorless H-$\mathbf{1}_2$ and colored H-$\mathbf{1}$ again and saw it confirmed by Schmidlin's observation.[36] This interpretation was backed by Wieland who recognized the similarity between the temperature dependency of the $N_2O_4 \rightleftharpoons NO_2$ equilibrium and the temperature dependency of the molecular weight of "triphenylmethyl". He postulated that only the radical character of H-$\mathbf{1}$ is responsible for the color and reactivity and makes the idea of mesomerism to a quinoid form unnecessary.[37]

The structural debate was settled in 1910, when Schlenk entered the field. Firstly, by the synthesis of the tri(4,4'-biphenyl)methyl radical **6** (Figure 6), which was the first fully dissociated, persistent, free organic radical;[38] this finally
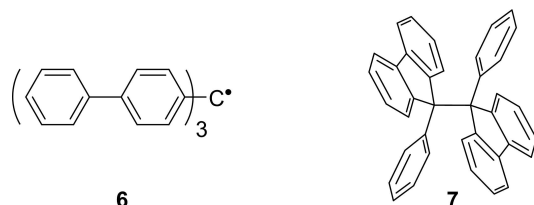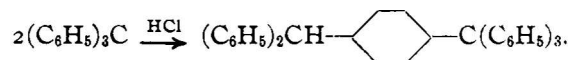
proved the existence of a free radical and made Gomberg's hypothesis of "triphenylmethyl" being the trityl radical fully plausible. Secondly, by demonstrating the possibility of isolating a stable HPE derivative, namely 1,1'-diphenyl-bisfluorenyl **7** (Figure 6).[39] Its synthesis was erroneously claimed by Gomberg in 1906,[27] but later **7** was obtained as a colorless solution which evidently consumed oxygen.[27] This back-bound HPE derivative dissociated only upon heating.

Further evidence was introduced by Piccard who recognized, based on deviations from Beer's law, that the equilibrium must be between a colored monomeric and a colorless dimeric "triphenylmethyl".[40] By disproving Schmidlin's "tautomerism" thesis,[35] further support for the H-$\mathbf{1}_2 \rightleftharpoons$ H-$\mathbf{1}$ equilibrium was thought to have been found.

Gomberg, however, warned: "Es ist in den letzten Jahren üblich geworden, die dimolekulare Form des "Triphenylmethyls" als Hexaphenyläthan zu bezeichen. So plausibel diese Ansicht auch von vornherein erscheinen mag, so dürfte es doch angebracht sein, daran zu erinnern, daß sie des experimentellen Beweises bis jetzt noch entbehrt" (It became common to consider the dimolecular "triphenylmethyl" as HPE. As plausible as this might look, it is advisable to remind oneself that this view lacks proper experimental evidence).[41] He still adhered to the quinoid structures and postulated the "equilibrium formula" in which all possible forms – the mesomers of TPM and HPE – were taken into account. This view is explained in depth in Gomberg's 1914 review about the initial years of "triphenylmethyl".[42] The existence of free radicals is established as "many analogues of triphenylmethyl are capable to exist". He recapitulates the most striking features of these radicals, namely color, autooxidation, and acid catalyzed re-aromatization: The color is indicative of two forms of "triphenylmethyl", a colored and an uncolored one in equilibrium with each other. "Triphenylmethyl" takes up oxygen with the eager of yellow phosphorus (the impure white allotrope). The acid catalyzed rearrangement of "triphenylmethyl" to Ullmann's hydrocarbon is depicted as a single step from H-$\mathbf{1}$ to **4** (Figure 7) without discussion of the mechanism or noticing its importance.

Gomberg reminds us of his dilemma: While the trivalent carbon was hesitantly accepted and the free TPM radical explains all the reactivity, the weight of "triphenylmethyl" corresponds to a dimer and gets lower with raising temperature. He concluded: "*Hexaphenylethane still remains a figment of the imagination. And so the idea began to take root more and more generally that, after all, there is no difference between the so-called "triphenylmethyl" and the hexaphenylethane, that the former is in reality the latter. [...] Henceforth*

Figure 6. The first fully dissociated free radical tri(4,4'-biphenyl)methyl radical 6 and the first stable HPE analog 1,1'-diphenyl-bisfluorenyl 7.

Figure 7. Gomberg's representation of the acid catalyzed re-aromatization. Reprinted with permission from ref.[42] Copyright (2021) American Chemical Society.

the hexaphenylethane constitution for triphenylmethyl began to appear in the literature more frequently[...]" But "*It is self-evident that such a constitution could at best account for the colorless triphenylmethyl alone.*" He summarized "triphenylmethyl" therefore as (Figure 8): While the equilibrium formula "is in full harmony with the facts known up to the present, [...] the explanation hexaphenylethane ⇌ triphenylmethyl [radical] is finding a wider acceptance largely because of its simplicity." This point of view ultimately would be accepted for the next five decades: Schmidlin's book about "triphenylmethyl" broadly reviews every aspect and treats solid "triphenylmethyl" as H-**1**$_2$ which upon dissolution "most probably" partly dissociates to the H-**1** radical.[43] Jacobson's structure **2** seemed out of question, even though he mentioned it as one of the other possibilities. Schmidlin saw nothing arguing against H-**1**$_2$. In 1916, Lewis explained organic radicals based on the electronic structure as molecules with an odd number of electrons.[44] He correlated the color of the radicals with the last, odd electron and rendered the quinoid mesomer of the "triphenylmethyl" monomer unnecessary. He agreed with an equilibrium between H-**1**$_2$ and H-**1** in benzene. In Gomberg's 1924 review, a quinoid mesomer of the monomeric species was still assumed to account for the color.[45] In the whole review, **2** was not mentioned, rather, an equilibrium between H-**1**$_2$, H-**1**, and quinoid **1'**. The structure of solid "triphenylmethyl" seemed accepted as HPE. The acid catalyzed rearrangement now occurred as a two-step process as postulated by Tschitschibabin and therefore the strongest chemical hint for the true structure of "triphenylmethyl" was disregarded. Soon after, even Gomberg accepted the structure of H-**1**$_2$ for solid "triphenylmethyl" because of its lack of color.[30a]

Physical Properties of "Triphenylmethyl"

In the following years, the question shifted from structure to properties. In 1929, Ziegler found the dissociation of "triphenylmethyl" to be in agreement with Ostwald's law of dilution.[46] The determined degree of dissociation of 3.6% corresponds to a heat of dissociation (ΔH_d^{293}) of -11.5 kcal mol^{-1}. For the first time, a quantification of the instability of dimeric "triphenylmethyl" was given. This value was later confirmed by Müller[47] and much later with the correct structural assignment by Neumann.[48]

In 1930, experimental rates of the oxidation of "triphenylmethyl" revealed the existence of a second reaction pathway, which leads to "the oil": The scavenging of oxygen by the radical and, and this was new, the direct oxidation of triphenylmethyl.[33b] Three years later, the concentration dependence of the direct oxidation of the dimer was discovered.[33a] Ziegler showed an inhibition of product formation by high concentrations of pyrogallol in the oxidation to the bis(trityl)peroxide. Only tritylhydroperoxide formed and, accordingly, one equivalent of O$_2$ had been consumed per trityl chloride. This revealed a stepwise oxidation. Unfortunately, Ziegler made no attempt to characterize the product of direct oxidation and the interpretation of "triphenylmethyl" as H-**1**$_2$ remained.

The ability to measure the magnetic susceptibility sparked attempts to gain new insights into the behavior of "triphenylmethyl" and its derivatives. Roy and Marvel found that with increasing "weight" of alkyl substituents in "all-*para* alkyl HPE" the degree of dissociation increased.[49] These finding are hardly explicable if one assumed a hexaphenylethane structure as steric and resonance effects are negligible in the *para* position. Indeed, the change in dissociation was later attributed to substituent effects on the molar magnetic susceptibility.[50] When Ziegler wrote a "Festschrift" about his 25th anniversary in radical chemistry in 1948, the H-**1**$_2$⇌H-**1** equilibrium and the successful synthesis of HPE had been fully accepted. In the review, the question was raised why the central carbon-carbon bond in HPE is so weak and resonance *vs.* steric effects were discussed. Both effects were said to work together: Resonance stabilizes the radicals while steric clashes lead to an elongated and therefore weak(er) "ethane" bond.[51] Around the time when the whole academic knowledge of the synthesis of HPE imploded, Schwartz synthesized a further back-bound, stable HPE derivative, bitriptycyl (**8**),[52] and Wittig and Schoch synthesized hexabenzo-[b.d.g.i.Z.n][4.4.4]propellamancene (**9**), an all-*ortho* cross bridged HPE (Figure 9).[53] No further questions on "triphenylmethyl" were asked.

A New Race Towards Hexaphenylethane

A landmark in the "triphenylmethyl" history was the 1968 publication of Lankamp, Nauta and MacLean, which once and for all proved the structure of dimeric "triphenylmethyl" as 1-diphenylmethylen-4-triphenylmethyl-cyclohexa(2,5)diene **2**,[54] the structure suggested by Jacobson in 1905.[19] They reinvestigated "triphenylmethyl" in terms of UV and NMR spectroscopy. Hence, "triphenylmethyl" showed peaks at 5.8
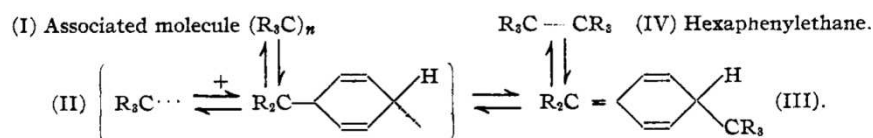
Figure 8. The "equilibrium formula" from Gomberg's 1914 review. Reprinted with permission from ref.[42] Copyright (2021) American Chemical Society.
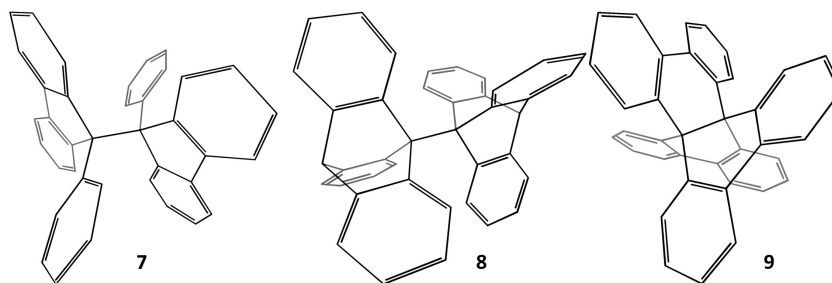
Figure 9. Perspective skeletal formulas of the back bonded or clamped HPE derivatives: 1,1'-diphenyl-bisfluorenyl 7, bitriptycyl 8 and hexabenzo-[b.d.g.i.Z.n][4.4.4]propellamancene 9.

to 6.4 ppm, assigned to the olefinic hydrogens, and a signal at 5 ppm, assigned to the *para*-methine hydrogen, in contrast to the expectation of a signal-free olefinic region in the ^{1}H NMR for true HPE.[54] The interpretation was confirmed one year later when Brunner synthesized an α-^{13}C derivative of triphenylmethyl chloride and investigated the corresponding dimer *via* ^{13}C NMR. Two resonances [62.6 (sp^3-C) and 137.3 (sp^2-C) ppm] were found indicative for the unsymmetric structure **2**. Further, ^{1}H NMR studies gave integrals of 4:1 for the signals at 6.4–5.8 and 5.05 ppm, respectively. All-*para* deuteration eliminated the resonance at 5.05 ppm and gave a clear AB system at 6.3 and 5.9 ppm with $J = 10.5$ Hz, in line with structure **2**.[55] Subsequently, the structure of "the oil" (the byproduct of the autooxidation of "triphenylmethyl") was determined as *para*-(hydroperoxidobenzhydryl)-tetra-phenyl-methane, which must originate from **2**.[30b] Ultimately, single crystal X-ray diffraction (SC-XRD) structures of **2** were determined by Allemand[56] and later by Blom.[57]

While evidence from spectroscopic tools like NMR might have been available only since the 1950s, pure chemical evidence – acid catalyzed re-aromatization, *para*-halogen lability and, if it had been analyzed, the structure and origin of "the oil" – pointed directly towards structure **2**.[30a] Hitherto, hexaphenylethane had never been synthesized and remained elusive. Therefore, the race towards the synthesis of an unbridged HPE had been reset by Nauta in 1968.

The First Unbridged Hexaphenylethane

In the 1970s, the structural properties of radicals were predominately determined *via* electron paramagnetic resonance (EPR) spectroscopy. The EPR spectrum of TPM was problematic to solve because of odd contributions at the *meta* positions. Based on previous findings that the introduction of ^{t}Bu groups drastically simplified EPR spectra,[58] Baer *et al.* synthesized and investigated all-*meta* ^{t}Bu TPM.[59] They found a negligible electronic influence by *meta* ^{t}Bu substitution and a twisting of 24 to 26° of the phenyl rings. These findings were later confirmed by Sakurai and coworkers.[60] Following the EPR resolution improving ability of all-*meta* ^{t}Bu substitution, Stein and Rieker synthesized the tri(2,6-di-*tert*-butyl-4-

biphenylyl)methyl radical (**10**) and also found "*no significant additional stabilization due to π-conjugation relative to [the all-meta 'Bu TPM radical]*".[61]

In 1978, Rieker *et al.* crystallized the first unbridged HPE derivative entitled "*Hexakis(2,6-di-tert-butyl-4-biphenylyl)ethane [10₂] – The First Unbridged Hexaarylethane*".[62] Baer *et al.* found monomeric crystals grown from benzene;[59] Rieker chose cyclohexane and obtained colorless crystals of **10₂**. While the determined SC-XRD proved the HPE structure (Figure 10), an oddly short ethane bond of $r_{CC} = 1.47$ Å was determined. This contradicted previous views of Ziegler[51] and empirical force field (EFF) computations of Mislow,[63] who predicted an elongated bond. Yet, Rieker explained the existence of **10₂** purely based on steric reasons: "*Steric hindering of formation of the Jacobson-Nauta structure by incorporation of bulky groups [in meta and para positions lead to the following picture: the TPM radical]*
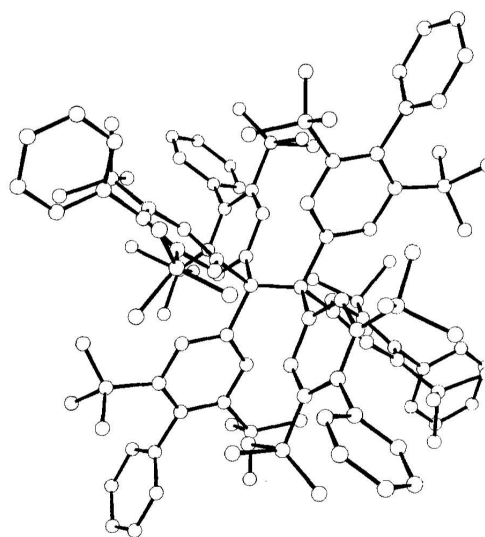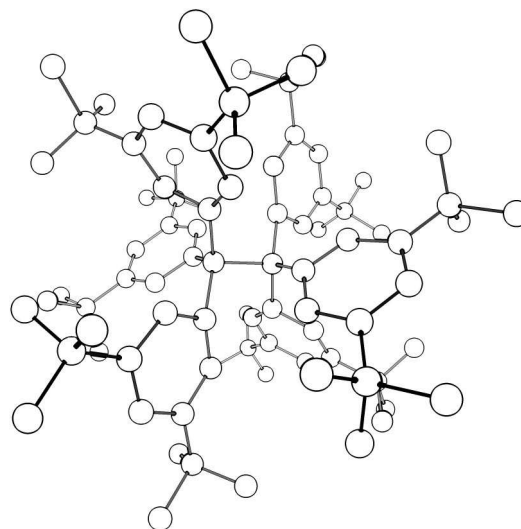

Figure 10. Molecular structure of hexa(2,6-di-*tert*-butyl-4-biphenylyl)ethane (**10₂**) determined *via* SC-XRD and as depicted by Rieker. Hydrogens were not shown. The central r_{CC} was determined as 1.47(2) Å. Reprinted with permission from ref.[62] Copyright (2021) John Wiley and Sons.

*must then either be persistent as the monomer – or dimerize
[...] to [HPE].*" Moreover, they found a decay of the HPE
signals over six days with a final degree of dissociation of
63 % for **10**$_2$ and 55 % for all-*meta* ^{t}Bu HPE (^{t}Bu-**1**$_2$). The
authors took this decay as a sign of a slow equilibration and
the assumed high activation barrier as a hint toward the
existence of an HPE derivative. Few spectroscopic data were
given; NMR spectroscopy gave no definitive conclusion
because of "*the high degree of dissociation and the sensitivity
of the radical towards traces of oxygen*". Still, a chemical shift
of 70.7 ppm was specified for the ethane carbons. In the end it
was claimed that "*The high melting point and slow dissocia-
tion of [**10**$_2$] would suggest that the unsubstituted hexaphenyl-
ethane should also be synthesizable.*"

In contrast to an unusual short central C–C-bond, Mislow
predicted a bond elongation in HPE on the basis of extended
force-field (EFF) computations.[63] A chiral D_3 eclipsed
conformation was found to be the ground state, being
2.55 kcal mol^{-1} lower in energy than an achiral S_6 staggered
conformation that had been found experimentally. Severe
strain between the trityl moieties was made responsible for a
drastically elongated r_{CC} of 1.64 Å in both conformers. Steric
arguments were also used by Rieker to explain the formation
of the ethane bond. As there were several bridged HPE
structures available,[39,52–53] Mislow commented: "*Neverthe-
less,[...] all compounds [...] with bond lengths greater than
1.6 Å are bridged to avoid [...] the molecule to fall apart.
Thus, the molecules survive despite the presence of what is
most likely a severely weakened bond. HPE does not enjoy
such bridging.*" Clearly a correlation between bond length and
strength is made: "*The stability of polyarylethanes correlates
well with r_{CC}[...]*". Rieker argued that the ^{t}Bu substitution
might lead to the bond shrinkage instead elongation.[62] As it
turned out later, *vide infra*, there is some truth in this statement
but with an entirely different causality.

As a result to Rieker's argument, Mislow revised his
former computations on HPE because of "*the dismaying
prospect of a major failure of the EFF method in the prediction
of a structure of central importance in chemistry.*"[64] At the
time the trust in theory was in many instances not high enough
to question an experiment. The efforts were extended to the
MMI, MMPI, and MM2 empirical force-fields as well as
semiempirical MNDO quantum mechanical computations on
HPE. Even EFF computations of the very large **10**$_2$ were
performed; "*the largest molecule ever calculated by a full-
relaxation EFF method*"[64] – and so any computational method
at that time.[65] The computational results all agree on an
elongated central C–C bond of more than 1.6 Å. Mislow
thoroughly confirmed his former results and declared a
reinvestigation of the SC-XRD to eliminate any doubts.

Five years later, Mislow and Kahr crystallized a truncated
10$_2$, namely all-*meta* ^{t}Bu HPE ^{t}Bu-**1**$_2$ (Figure 11).[66] The
crystallization took over two months. Still, the crystals showed
severe disorder similar to other hexa-homosubstituted ethanes.
The outer phenyl substituents were heavily influenced by this
disorder (Figure 11). Nonetheless, the central bond length was

Figure 11. Molecular structure of hexa(3,5-di-*tert*-butylphenyl)ethane
^{t}Bu-1$_2$ determined *via* SC-XRD by Mislow[66] taken from the CSD (No.
1153536).[68] The r_{CC} was determined as 1.67(3) Å. Hydrogens and
disorders were omitted for clarity. The odd angles around the *ipso*-
carbons arise from the disorder.

unambiguously determined to be 1.67(3) Å in line with
previous computations. In 1988, Mislow and Kahr again
published new evidence to account for the lack of biphenyl
groups in earlier studies. Because they were unable to obtain
suitable crystals for SC-XRD, nutation NMR spectroscopy
was performed on powders. α-^{13}C Derivatives of **10**$_2$ and ^{t}Bu-
1$_2$ were synthesized and ^{13}C–^{13}C distances of 1.64–1.65 Å
were determined in both cases. With this, Mislow summarized
that "*[...] two independent experimental and one computa-
tional determination of [r_{CC}] comprise a set of values with
surprisingly little variance. [...] These results remove any last
doubt that the previously reported central bond distance is
grossly in error.*"[67] Hence, theoretically well-founded compu-
tations provided the impetus to redo an experiment and
eventually correct a very significant error. One key question
was not asked by Mislow and Kahr: why is ^{t}Bu-**1**$_2$ isolable
while much less crowded H-**1**$_2$ is not? What is the origin of the
stabilization through the ^{t}Bu groups?

It was not until 14 years later, when HPE found its way
back into the literature by a computational analysis of Vreven
and Morokuma, who re-computed the structure of H-**1**$_2$ with a
three-level hybrid quantum mechanical ONIOM method.[69]
With a computed BDE of 16.6 kcal mol^{-1}, the synthesis of
HPE seemed feasible. But, as Lewars later put it: "*The
problem with making hexaphenylethane likely lies not with the
instability of this molecule, but rather with the preference of
the triphenylmethyl radical to dimerize faster to the meth-
ylenecyclohexadiene than to the hexaarylethane. This is a
kinetic effect probably arising from less steric hindrance in the
transition state for formation of the methylenecyclohexadiene:
this dimerization mode is less disfavored by nonbonded (steric)*

interactions than is the 'end-on' dimerization of Ph₃C + CPh₃."[65]

Vreven and Morokuma found a r_{CC} of 1.72 Å which is longer than the reported experimental values for the more crowded HPEs.[66–67] Referring to strain as the major reason for the long r_{CC} and therefore the instability of HPE, they were unable to rationalize this deviation in r_{CC} and attribute it to the "soft central bond" being compressed by crystal packing effects.

London Dispersion Interactions in Hexaphenylethanes

Mislow et al. as well as Vreven and Morokuma attributed a "*great internal strain and long (therefore weak) central C–C bond*" to HPE; seemingly steric clashes are responsible for the failure of all synthetic attemps.[63,65,69] According to Rieker, steric clashes are also responsible for the ethane bond formation as "*Steric hindering of formation of the Jacobson-Nauta structure [10] must then either be persistent [...] or dimerize to 10₂.*"[62] Another instance of steric clash was found when Neumann *et al.* disproved earlier findings[49] that increased bulkiness of all-*para* alkyl substituents at TPM radicals leads to more facile dissociation of the "HPEs": "*Eine Dimerisierung der Radikale findet also nicht statt. Denkbar war zumindest in einem Teil der Beispiele eine Chinoidbildung [...]. Das ist nicht der Fall. Selbst bei kleinen Resten wie F oder CN wird dem ein unüberwindbarer Widerstand entgegengesetzt. [...] Weiterhin hätte, wie im Falle des Tris(3,5-di-tert-butyl-4-phenylphenyl)methyls 10₂ bei einfacher para-Substitution nun doch vielleicht das ethanartige α,α-Dimer auftreten können. Auch das ist nicht der Fall*" (The radicals do not dimerize. At least in part of the examples a quinoid dimerization can be envisioned. This is not the case. Even small substituents such as F or CN introduce an insurmountable resistance against dimerization. Further, in analogy to 10₂, simple *para* substitution could lead to an ethane-like α,α-dimer. Again, this is not the case).[50]

Steric clashes refer to Pauli (exchange) repulsion of molecules or moieties in finite proximity. This is a *destabilizing* effect. In this sense, steric strain destabilizes HPE and an equilibrium between the less strained JNS and free radicals was observed. Steric shielding of the *para*-positions by *para* substitution also destabilizes the JNS through increased strain and persistent TPM radicals are observed. Steric shielding of the *para*-positions by all-*meta* substitution leads to an isolable HPE. This observation could arise from a destabilization of not only the JNS but also of the radicals. Destabilization of the TPM radicals could occur by a decreased delocalization of the unpaired electron *via* increased twisting angles of the phenyl rings or electronic substituent effects. Both are experimentally not observed as the twist angles in TPM (26.5°)[70] or all-*meta* ᵗBu TPM (24–26°)[59] are similar and *meta* alkyl substitution has a minor effect on the radical stability.[71] Therefore, the question arises whether there is a *stabilizing* effect that could explain the increased stability of ᵗBu-1₂. Note that it is the

opinion of the present authors that it is much more satisfying to identify stabilizing interactions than destabilizing factors; it is also didactically easier to convey.

A step in the right direction was taken by Dames *et al.* in 2010.[72] For the first time, parent H-1₂ was examined with a computational method that included considerable mid-range electron-correlation effects at the M06-2X/6-31+G(d,p) level of theory, thereby also capturing an appreciable amount of London Dispersion (LD). A r_{CC} of 1.70 Å and a BDE of 11.6 kcal mol⁻¹ was determined (11.3 kcal mol⁻¹ *via* an iso-desmic equation) in agreement with Vreven and Morokuma.[69] In contrast, B3LYP (which is not geared toward inclusion of medium to long-range electron dispersion effects, including LD) failed to describe the BDE (−23.8 kcal mol⁻¹).[73] In light of this, "*The central C–C bond strength [is] a result of competition between steric repulsion and dispersive attraction.*"

Insertion: Long Known but Long Neglected London Dispersion Interactions

The importance of attractive intermolecular forces was already noticed by Johannes Diderik van der Waals (vdW), a Dutch physicist, in 1873. Severe deviations from the ideal gas law were apparent at that time. Therefore, vdW developed a simple but intelligible correction through the incorporation of microscopic properties to the macroscopic ideal gas law to account for the deviations to model real gases. The vdW equation allows, in contrast to, e.g., the virial expansion, for a direct comprehension of molecular expansions and interactions. These interactions and the behavior of compounds in all states can be understood on the basis of electrostatic interactions between (in shape and charge distribution anisotropic) molecules. Hence, Coulomb, Keesom, and Debye interactions are readily explained by static charges, dipoles or higher multipoles. The existence of condensed matter for most molecules is rationalized on the basis of these classic electrostatic interactions. Still, none of these interactions explain the appearance of a condensed phase for, e.g., noble gases.

A novel, non-classic, quantum mechanic, attractive, long range interaction ($\sim r_{ab}^{-6}$) was found in a perturbative description of two hydrogen atoms at "large" distances by London and Eisenschitz in 1930.[74] "*Man wird diese [...] Anziehungskräfte in Zusammenhang mit den van der Waalschen a-Kräfte bringen*" (One will connect these attractive forces with the parameter **a** from the van der Waals forces). In their rigorously derived perturbation matrix the second off-diagonal elements were attributed to a resonance effect. Here, a virtual double excitation takes place: Transitions have dipole moments which mutually attract each other.[75] These excitations arise from "*virtuelle periodische Bewegungen*" (virtual periodic movements), later referred to as zero-point motion.[76]

In the subsequent publications London developed an extensive systematization of the vdW interactions – Keesom, Debye, and dispersion – and introduced further approxima-

tions for the latter.[77] The magnitude of the transition dipole moments should be derived from the oscillator strength f within the framework of the dispersion of light because *"[...]diese Wirkungen, die man selbst für die einfachsten Moleküle kaum je wird direct berechenen können[...]"* (these dipole moments are barely directly calculable, even for the smallest molecules). Hence, London called these interactions dispersion forces. Since even values for f had not been determined then, the isotropic polarizability α was used instead. Further, as a workaround for the unknown "virtual" excitations energies for the noble gases, London assumed an interval between the first excitation energy and the ionization energy I_E. It appeared that the calculated **a**-values corresponding to the I_E agreed well with the experimental **a**-values and the dispersion energy E_{Disp} was reasonably described for noble gases by:

$$E_{Disp} = -\frac{3}{4}\frac{I_E\alpha^2}{r_{ab}^6} \qquad (1)$$

Already at this early stage, London noticed that for many molecules, E_{Disp} dominates intermolecular interactions. London states: *"It is seen that the induction effect is in all cases practically negligible, and that even in such a strong dipole molecule as HCl the permanent dipole moments give no noticeable contribution to the van der Waals attraction. Not earlier than with NH₃, does the orientation effect become comparable with the dispersion effect, which [...] seems in no case to be negligible."*[76]

Unfortunately, these insights and rationalizations were by and large not accepted or even acknowledged in the chemistry community. With the appearance of SC-XRD, CPK models, force fields and highly approximate quantum mechanical methods the focus continually shifted to the "directly" accessible interactions like steric effects *via* bond length and angle deformations as well as electrostatic interactions like hydrogen bonding or "π-π stacking" attributed to certain functional groups. Hunter cunningly points this out when writing: *"When molecular scientists obtain an unexpected result in a system, they tend to invoke the mythical powers of the 'π-π interaction', 'π-stacking', 'charge transfer' (CT), 'π-acid/π-base' or 'electron donor acceptor (EDA) interaction'."*[78] Note that the interaction of benzenes is governed predominantly by LD.[79] The notion of LD as a small force between small particles supported its massive underestimation.[80] Long accepted and often used density functional theory (DFT) implementations (e. g., B3LYP), frequently employed because of their moderate scaling of computational demand whilst providing direct insights into chemical properties,[81] inherently truncate electron correlation effects and therefore lack the inclusion of LD.[82] It was noticed early that certain popular combinations might cause favorable error compensations and give *"the right answer for the wrong reasons"*.[83]

The failure of such widely applied now considered early DFT computations surfaced and the importance of LD gained

large attention recently.[80,84] This renewed interest in LD is supported by computational developments which enable us to dissect noncovalent interactions and reveal the significance of LD. Among these are symmetry adapted perturbation theory (SAPT),[85] switchable DFT dispersion corrections (DFT-D),[86] and the local energy decomposition (LED),[87] to only name but a few.

While it is generally accepted that LD governs the interaction of uncharged molecules in the gas phase and solid state, there are questions about the meaning and importance of LD in solution. While Hunter questioned stabilizing LD solute-solute interactions in general,[88] Cockroft *et al.* state regarding the difference between measured and theoretical unfolding energies of a double alkyl substituted Wilcox balance[89] that: *"The most likely explanation for the order of magnitude difference between the very small alkyl-alkyl interaction energies measured in this study and the large energies derived from enthalpies of vaporization and computational methods is that dispersion forces are effectively cancelled by competitive dispersion interactions with the solvent,[...]."*[90] This difference is most likely caused by the multiple conformers of the long alkyl chains which are in equilibrium with each other at r.t. that are not taken into account of in Cockroft's computational analysis. This cancelation also contradicts Wilcox's earlier notion of the importance of LD in his balance.[91] Shimizu found not a cancelation but just an attenuation and *"Aromatic surfaces still form attractive dispersion interactions in solution just as they do in vacuo."*[92] A recent experimental comparison of the very same species in gas phase and solution by Chen and co-workers did not show a cancelation but also an attenuation. The study of solvent effects on intramolecular dispersion were also pursued in the Schreiner group by using the valence bond isomer equilibration of 1,4- and 1,6-di-ᵗBu-cyclooctatetraene in 16 different solvents.[93] In the folded 1,6-isomer, the two ᵗBu-groups are at an H···H distance of about 2.5 Å but they are well separated in the unfolded 1,4-isomer (H···H distance ≈ 7 Å). Temperature-dependent nuclear magnetic resonance measurements on the equilibrium positions in these solvents reveleal that the folded isomer *always* is preferred. Energy decomposition analyses at the density functional and *ab initio* levels emphasize the predominance of LD interactions enthalpically, to arrive at the conclusion that intramolecular LD interactions not cancel in solution.

Hence, a significant amount of LD transfers from the gas phase into solution;[94] this is a general observation.[95] Astonishingly, LD even significantly contributes in highly polar media[96] or even in dimers of equally charged species.[97] In light of the importance of LD for molecular structures it is striking how a purely steric view on HPE could remain for over 100 years.

Perspective

Solving the Hexaphenylethane Riddle

The question about the singularity of isolable all-*meta* ^tBu substituted HPE derivatives 10_2 and ^tBu-1_2 or stable, unbridged and yet very elongated sp³-sp³ C–C bonds in general was approached by Schreiner and Fokin in 2011, when they discussed the bond length-bond strength correlation:[98] "*[...]shorter bonds are considered stronger, and vice versa. However, there are many exceptions [...]*" and "*The general recipe for elongating chemical bonds involves steric crowding. [It] reaches its limit of applicability with the highly crowded 'classic riddle' hexaphenylethane, which has not yet been realized [...],*" and, finally, "*Such compounds can be realized by shifting the energy balance in favor of attractive dispersion interactions that outweigh to a large degree the repulsive dispersion contributions leading to C–C bond elongation.*" This was very true for the isolable all-*meta* ^tBu HPE. This was the starting point for Grimme and Schreiner reconsidering the work of Dames et al. to answer the ultimate question why especially all-*meta* ^tBu TPM, but not all-*para* ^tBu TPM or TPM itself α,α-dimerizes: "*How can the derivative of a molecule that dissociates owing to steric hindrance become stable by increasing steric bulk?*"[99] At TPSS-D3/TZV(2d,2p) (including LD "D3"-corrections) HPE is computed to spontaneously dissociate ($\Delta G_d^{298} = -9$ kcal mol⁻¹) and recombine as JNS. A stability gain *via* the ^tBu in all-*para* ^tBu HPE (11_2) is "*practically absent*", the molecule also spontaneously dissociates ($\Delta G_d^{298} = -7$ kcal mol⁻¹) but *para* substitution prevents JNS formation and therefore all-*para* ^tBu TPM is fully dissociated and persistent as a radical.

Contradictory to Mislow's statement that "*the tert-butyl groups have no special effect on the bonding parameters of hexa(2,6-di-tert-butyl-4-biphenylyl)ethane*",[64] the computational analysis revealed that the major reason for the stability of ^tBu-1_2 ($\Delta G_d^{298} = +13.7$ kcal mol⁻¹) is LD between the ^tBu groups ($E_{disp} = 40$ kcal mol⁻¹).[100] More elaborate PWPB95-D3/QZVP(g,f) computations with solvent corrections predicted (in the true sense of the word, i.e., foresaw) a ΔG_d^{298} in the range of −3 to +1 kcal mol⁻¹. Further, the dissociation curve of ^tBu-1_2 revealed a second minimum, revealing a vdW complex (^tBu-$1)_2$ similar to the Schlenk radicals.[101] Grimme

and Schreiner concluded that "*the overall repulsive phenyl-phenyl interactions in HPE are overcompensated in all-meta ^tBu HPE by addition [of] tert-butyl groups that serve as 'dispersion energy donors' [...].*" These are now commonly referred to as "DEDs" (Figure 12).

## Dissociation of Hexaphenylethanes

We published our first experimental results about ^tBu-1_2 at the end of 2016.[102] The goal was to gain deeper experimental insights into the bonding situation between the two TPM halves in ^tBu-1_2, especially considering the influence of *intra*molecular LD interactions. As Vreven and Morokuma put it 14 years earlier: "*A key question in HPE chemistry is the binding energy of the symmetric dimer*".[69] Remarkably, the hindered rotation of the phenyl rings in ^tBu-1_2 leads to a distinctly different chemical environment for the "off-*ipso-para*-axis" moieties. In the NMR spectrum, the *ortho*-hydrogens as well as the *meta*-^tBu groups split into doublets, whereby the former experience a large 1038 Hz and the latter a smaller 18 Hz split. We observed a chemical shift of $\delta = 71.5$ ppm (C_6D_{12}) for the central α-carbons, in line with Rieker's 70.7 ppm[62] (C_6D_6) and the extrapolation of the α-¹³C shifts of 1,1,1-triphenylethane, 1,1,1,2-tetraphenylethane and 1,1,1,2,2-pentaphenylethane (69(3) ppm[103]).[104]

To obtain the first experimental value for the free dissociation energy of ^tBu-1_2 and probe the earlier computational predictions, we performed variable temperature NMR experiments. The corresponding van 't Hoff plot showed a strong temperature dependence on the ^tBu-1_2 and ^tBu-1 concentrations and gave $\Delta G_d^{298} = -1.60(6)$ kcal mol⁻¹, in good agreement with true computational predictions of Grimme and Schreiner of 2011.[99] Theory had reached a stage where it could make a bold prediction that could be tested experimentally and confirmed to be correct.

A computational study (B3LYP-D3(BJ)/cc-pVDZ) on all-*meta* alkyl substituted HPE derivatives (R-1_2) – not corrected for the possible dynamic transitions of close lying low energy structures due to rotation of lower symmetry alkyl moieties – revealed a good correlation between the polarizability α, hence
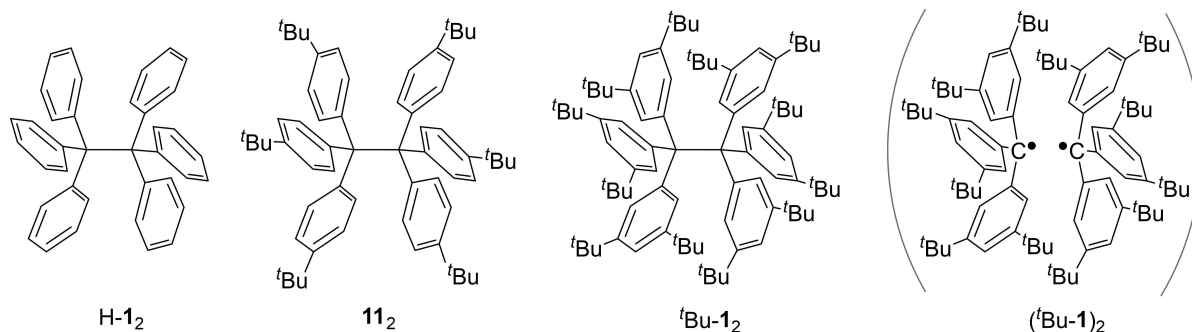
Figure 12. Molecular structures of HPE H-1_2, all-*para* ^tBu HPE 11_2, all-*meta* ^tBu HPE ^tBu-1_2 and the vdW triplet complex of two all-*meta* ^tBu TPM radicals (^tBu-$1)_2$.
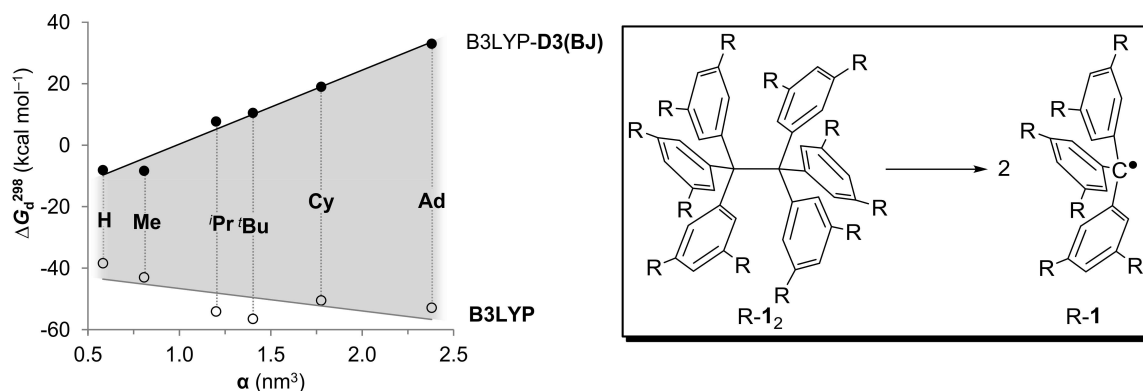
Figure 13. Correlation between the increasing free dissociation energies (ΔG_d^{298}) of R-1$_2$ to 2 R-1 determined by B3LYP-D3(BJ)/cc-pVDZ and the increasing computed polarizabilities (α) with substituent size is found (R^2 = 0.98). The opposite, but slightly worse correlation is found for dispersion-uncorrected B3LYP/cc-pVDZ computations. The grey area indicates the E_{disp} acting between the molecular moieties.

correlating LD interactions as well, and ΔG_d^{298} (Figure 13). The increase in LD interactions was also visually confirmed by NCI[105] plots. These derivatives therefore might serve as excellent molecular balances[106] to experimentally probe LD between the *meta* alkyl moieties presumably acting as DEDs.[99]

In the following year, we found all-*meta* ^{t}Bu triphenyl-methane (**12**), formally the hydrogenation product of ^{t}Bu-**1**$_2$, to crystallize in a head-to-head dimeric arrangement **12**$_2$ (Figure 14).[107] The SC-XRD featured a short C–H···H–C contact of the central C–H moiety. Using neutron diffraction (NRD) measurement of a large crystal (3.6×4.4×4.6 mm) of **12** at temperatures as low as 20 K confirmed the hydrogen atom positions in **12**$_2$ accurately. The NRD structure revealed an $R_{H\cdots H}$ of 1.566(5) Å – the shortest C–H···H–C contact reported to date. This head-to-head arrangement was recently also confirmed via ionization loss stimulated Raman spectroscopy in molecular beam experiments to resolve structure sensitive vibrations. Hence, the arrangement is not result of crystal packing and as it prevails in the gas phase,. The head-to-head arrangement is maintained even under isolated molecular beam conditions in the absence of packing effects of the solid state. The peculiar head-to-head arrangement therefore must result from extraordinarily strong LD interactions. The central Raman-active aliphatic C–D vibration of methine-deuterated ^{t}Bu-**1**$_2$ is associated with an unusually short C–D···D–C distance as revealed by the strong blue-shift compared to the unperturbed case. As a counterexample, the dimer of unsubstituted triphenylmethane displays an approximately S_6-symmetric tail-to-tail arrangement.

The massive mutual penetration of the electron density – the contact is 35% shorter than the sum of their vdW radii (2.4 Å[108]) and more than half way to covalent H–H – causes large Pauli repulsion, which must predominantly be counterbalanced by the only available attractive interaction, namely LD. It was shown that the ^{t}Bu groups again act as DEDs and contribute decisively to the compression of the vdW complex. This peculiar dimer gained widespread attention.[109]
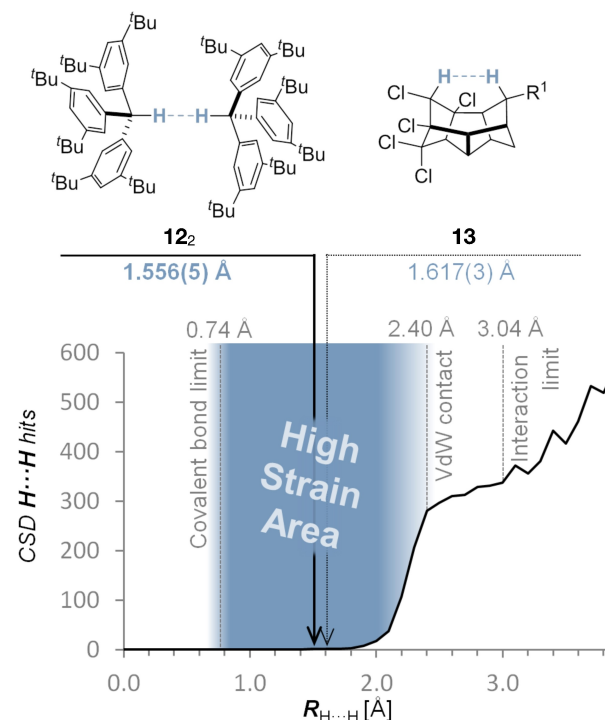
Figure 14. Top: Skeletal structures of dimeric 12$_2$ (left) with its short H···H contact and former record holder "Half-Cage" 13 (right, R^1: OBn).[110] Bottom: Hits for H···H contacts determined by NRD in the Cambridge Crystal Structure Database (V5.38 + 2 Updates) increase quickly starting from distances around the sum of the van-der-Waals (vdW) radii of hydrogen. The high energetic range below R–H···H–R < 1.9 Å contains only seven non-bonded H···H contacts in six molecules revealing the difficulties to obtain such short contacts. Reprinted from the Annual Report of ILL 2017, Institut Max von Laue - Paul Langevin (ILL).

Recently, we expanded our efforts and synthesized a series of all-*meta* hydrocarbyl substituted TPM radicals (R-**1**; R = Me, ^{i}Pr, ^{t}Bu, Cy, Ph, Adamantyl = Ad) to experimentally corroborate our previous computations on the stability of the

corresponding HPE derivatives (R-**1**$_2$).[111] Over the course of these studies we also synthesized and characterized the alcohols [TPM-OH (R-**14**)], hydrocarbons [TPM-H (R-**15**)], halides [TPM-X (R-**16**)] and peroxides [(TPM-O)$_2$ (R-**17**)]. Several head-to-head dimers akin to **1**$_2$ were found in SC-XRD for alcohols R-**14** and hydrocarbons R-**15**. The hydrocarbon dimers Me-**15**$_2$, **1**$_2$ (=^{t}Bu-**15**$_2$), and Cy-**15**$_2$ feature short C–H···H–C contacts. In Me-**15**$_2$ the contact is only 13% shorter than the sum of the vdW radii (2.4 Å[108]), in Cy-**15**$_2$, the contact is even 24% shorter.[112] The record holder **1**$_2$ displays a distance which is decreased by 35%. This supports the proficiency of the ^{t}Bu moiety as a DED. Size, shape, and fitting effects where indicated by NCI plots of the molecular structures of R-**17**.

A large energetic deviation from the initial qualitative computational estimations to experiment compelled us to expand and improve the computations. The application of a triple-ζ basis set reduced superposition errors and a possible vdW radical complex (R-**1**)$_2$ as well as the JNS (R-**2**) were taken into account. A ΔG_d^{298} of -1.8 kcal mol^{-1} for ^{t}Bu-**1**$_2$ was determined, in excellent agreement with experiment.

Besides the known ^{t}Bu-**1**$_2$, we were able to identify Ad-**1**$_2$ via NMR by induction. Because the radical peak of Ad-**1** was obscured, a mathematical solution was established to directly determine ΔH_d^{298} via the temperature dependence of solely the Ad-**1**$_2$ peaks; ΔG_d^{298} was obtained a posteriori. The method was validated with known ^{t}Bu-**1**$_2$ and showed reasonable agreement. Ad-**1**$_2$ is more stable ($\Delta G_d^{298}=2.1(6)$ kcal mol^{-1}), qualitatively in line with our computational predictions and on the basis that Ad is larger and more polarizable than ^{t}Bu. The deviations between experiment and computations were attributed mostly to having to approximate the solution phase with a continuum solvent model. As no other R-**1**$_2$ was observed, only ^{t}Bu-**1**$_2$ and Ad-**1**$_2$ are stabilized enough by their substituents. Because ^{t}Bu and, even more so, Ad are expected to act as excellent DEDs and computations show a decisive role of LD in these R-**1**$_2$, we must conclude that LD indeed governs the stability in all-*meta* hydrocarbyl hexaphenylethanes. This realization should have consequences in the way we look at many other crowed structures and it forces us to reconsider many of the common "steric strain" interpretations to interpret structures and mechanisms.

This view had not been generally accepted before our work appeared. Allinger tested his MM4(2015) molecular mechanics force field with overcrowded molecules including **11**$_2$.[113] While it is recognized "*[...]that the forces that determine these bond lengths [are] i.e., stretching, bending, torsional, van der Waals, and electrostatic [...]*" it follows that "*Long C–C bonds are [...] mainly the result of steric effects [...].*" It is surprising that the question was not asked why these molecules exist after all, not to speak of an explanation what stabilized them. Suzuki *et al.* retained the notion that steric shielding of the *para*-positions in HPE is most important for the synthesis of all-*meta* ^{t}Bu HPE, with LD is only an add-on: "*When the formation of the JNS is prevented by the attachment of bulky substituents on the aryl moieties, HPE*

derivatives can be generated, which also gain stability by dispersion forces."[114]

Yet, there is plenty of evidence of the importance of LD regarding the stability of **10**$_2$ and ^{t}Bu-**1**$_2$. Corminbœuf and Sherrill tested their intramolecular symmetry adapted perturbation theory (ISAPT) on H-**1**$_2$ and ^{t}Bu-**1**$_2$.[115] They performed an energy decomposition and used it for comparison of these two molecules at fixed C–C bond distances of r_{CC}(H-**1**$_2$)= 1.713 Å or r_{CC}(^{t}Bu-**1**$_2$)=1.661 Å and found that in both cases (short and long r_{CC}) the gain in dispersion overcomes the repulsion and therefore ^{t}Bu-**1**$_2$ is more stable. Meitei and Heßelmann used H-**1**$_2$ and ^{t}Bu-**1**$_2$ as test systems for their incremental molecular fragmentation (IMF) method and obtained results very similar to those of Grimme and Schreiner, and Dames *et al.*,[116] namely, that the gain in LD from parent to substituted HPE is larger than the increase in repulsion. Ackermann, Breugst, and coworkers point out: "*For a long time, large and bulky substituents have intuitively been considered to act through unfavorable steric interactions, although London dispersion – the attractive part of the van-der-Waals interaction – is known for more than 100 years. The stabilizing nature of C–H···H–C interactions and their importance for organic transformations has only been fully realized within the last decades. Among others, these interactions explain the hexaarylethane riddle and [the] very short H···H contacts in tris(3,5-di-tert-butylphenyl)methane.*"[117] Ultimately, Boeré *et al.* state very appropriately: "*[...]Dispersion interactions [...] between 3,5-di-tert-butylphenyl groups [...] supplying more energy towards holding the sterically challenged all-meta tert-butyl hexaphenylethane together than the C–C covalent bond.*"[118]

Proclaimed Syntheses of Hexaphenylethane

It is clear that none of the scientist who claimed to have synthesized HPE before Nauta's publication[54] in 1968 could have known to have synthesized in fact another structure. However, there are several proclaimed syntheses of parent HPE after 1968 without convincing or even fabricated spectroscopic evidence. Common to these publications is that they synthesized HPE *en passant* without giving any indication of the importance to the synthesis of such a historically important molecule.

In this regard, Alper and Prince mentioned HPE in 1980 in a very short communication about the mild desulfurization of trityl thiol.[119] As a byproduct a dimer written as "RR" is obtained in 8% yield of isolated product! This could also correspond to the JNS (which still would be very sensitive to handle). But the CAS No.1117854-07-8 named "RR" in the follow-up publication by Alper three years later[120] corresponds to HPE that was produced in 38% yield. Neither publication comments on the "HPE" synthesis nor is a spectroscopic analysis provided. In another mild desulfurization in 1998 by Yu and Verkade no room for doubt was left as "*Substrate 16 underwent a similar reaction to generate*

triphenylmethane and hexaphenylethane", the latter in 27% yield.[121] Again, no analysis of the product was given. The latter procedure was used to synthesize this "HPE" and found its way into the literature again in "Mesolysis of Radical Anions of Tetra-, Penta-, and Hexaphenylethanes" by Majima in 2013.[122] The bond dissociation process of this "HPE" is broadly discussed and in the experimental section is stated that "*1,1,1,2,2-pentaphenylethane (Ph$_5$E) and 1,1,1,2,2,2-hexaphenylethane (Ph$_6$E) are known compounds*". Incidentally, the quoted reference for the synthesis of these two does not mention HPE.[123]

Rheingold and Trogler published the synthesis of azidobis-(pentamethylcyclopentadienyl)-vanadium(III) [η^5-C$_5$Me$_5$)$_2$VN3] by treatment of (η^5-C$_5$Me$_5$)$_2$V with sterically hindered azides.[124] "*For the case of N$_3$CPh$_3$, Pasteur separation and IR analysis (comparison with authentic samples) proved the blue crystals to be [η^5-C$_5$Me$_5$)$_2$VN3] and the pale-yellow crystals were Ph$_3$CCPh$_3$.*" No spectral data were provided. Similarly, "HPE" was obtained in a three-step procedure in 9% yield as a side product in the construction of tetrasubstituted carbons from carbonyl compounds with low-valent vanadium complexes.[125] Again, no spectral proofs were provided.

The most recent claim of having made HPE was published in 2017 by Liu et al.[126] In this publication Table 2, entry 16, depicts the synthesis of HPE by a nickel catalyzed reductive coupling. Most remarkably, the melting point as well as NMR data were provided in the supporting information: "*white solid; m.p. 230–233°C (lit. 2227[recte 222.7]-230°C);^{10} ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.97–7.30 (m, 30H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 131.2, 129.4, 128.4, 128.2, 127.3, 126.2, 125.8, 56.4.*" While the ^{1}H NMR chemical shifts appear plausible, the number of ^{13}C signals is dubious. Named are eight, while five or seven are expected, depending on whether there is free rotation of the phenyl groups or not, respectively. Further, the chemical shift of 56.4 ppm appears to be shifted upfield relative to tetra- and penta-phenylated ethanes.[104] Also, the reference for the melting point is given as "[10] R. binaghi[sic!], *Gazzetta Chimica Italiana* **1923**, 53, 879–887" – which clearly does not describe HPE.

But the story continues. The corresponding HPE NMR spectra in the Supplementary Information revealed crude manipulations as some apparently unwanted peaks were simply cut. This was discovered and communicated to us by Robert Mayer from the Ludwig-Maximilians-Universität München who submitted a comment of Liu's paper to the same journal. The handling editor did not allow this comment to be published and instead urged us to contact the authors directly. Ultimately a corrigendum was published which corrects the HPE structure (H-**1**$_2$) to Ullmann's hydrocarbon **4**.[127] The corrigendum finishes with a remarkable comment: "*The spectra editing does not affect the integrity of the research and conclusions of the published paper.*" We learn that for some authors and journal editors it now is apparently acceptable to edit NMR spectra to remove unwanted peaks.

While the synthesis was unproven proclaimed several times after 1968, to the best of our knowledge, parent H-**1**$_2$ remains elusive.

Outlook on Making Hexaphenylethane

The synthesis of HPE is still an open challenge. Its story is one of serendipity, wishful thinking, and human failure. Some synthetic attempts beyond a Wurtz type coupling of trityl halides were performed by Anschütz[128] and Kahr.[129] Anschütz thermally extruded CO$_2$ from the ester **18** (Figure 15a), but most likely observed Ullmann's hydrocarbon **4**.[65] Kahr attempted to make use of the crystal structure of trityl iodide, which crystallizes in a shifted head-to-head fashion. Solid state decomposition was expected to lead to HPE *via* a simple Walden inversion (Figure 15c). Unfortunately, thermal decomposition started only beyond 100°C and HPE could not be identified. Lewars also named further extrusion precursors,[65] but the problem of a rearrangement of labile H-**1**$_2$ to the JNS **2** under common reaction conditions remains.

A way to exclude rearrangements and facilitate the isolation of H-**1**$_2$ would perhaps be encapsulation. At the conditions of thermal extrusion of CO$_2$ in solution, more than enough energy is present in the system to split, dissociate and rearrange H-**1**$_2$ to **2**. If **18** is volatile enough to be evaporated and isolated in, e.g., a noble gas matrix under cryogenic conditions, extrusion could be induced by irradiation. Full dissociation of the reaction products is excluded by the solid
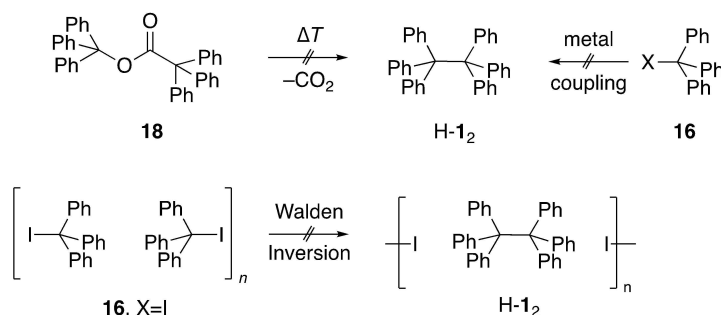
Figure 15. Synthetic attempts at hexaphenylethane by a) thermal extrusion, b) reductive coupling by metals or c) Walden inversion.

matrix. The change in shape and size during the extrusion is small it should proceed readily. Nonetheless, the large shape change from H-**1**₂ to **2** might impede the rearrangement (Figure 16). The low temperatures as well as the fast relaxation of hot states should promote the bound HPE state. Extrusion of N_2, CO, or SO_2 from bis(trityl)diazene **19**, hexaphenylacetone **20**, or bis(trityl)sulfone **21**, respectively, would proceed in the same fashion, but these are themselves elusive.[130]

The unknown **19** might be stable in an LD-shell akin the stable all-*meta* alkyl substituted bis(trityl)peroxide derivatives. The weak O–O bond is stabilized by the surrounding DEDs against Wieland[131] rearrangement. Similarly, the labile −N=N− fragment would experience stabilization.

This stabilizing effect of the LD-shell could also lead to a quantification of LD in all-*meta* alkyl substituted bis(trityl)peroxides or bis(trityl)diazenes. The onset of the Wieland rearrangement or N_2 extrusion should depend on the strength of the LD interactions between the substituents similar to R-**1**₂. Lastly, EPR investigations of the radical solutions of R-**1** in subcooled toluene similar to experiments by Broser[101] might reveal the dimeric vdW complexes (R-**1**)₂ and provide evidence for the predicted "bond length isomerism".[99]

Conclusions

Hexaphenylethane has a multifarious history, but has remained elusive to date primarily because of its instability due to the steric clashes between the trityl moieties and the resulting weak central C–C bond. As very crowded HPE derivatives such as those with *t*Bu and adamantyl groups in the all-*meta*

positions, however, can be spectroscopically identified even in solution, parent HPE is, in a cheeky way, "not sterically crowded enough", thereby lacking the positive aspects of large bulky groups: London dispersion. This key aspect was proposed by Grimme and Schreiner on the basis of DFT computations with and without dispersion corrections, ultimately leading to the concept of dispersion energy donors (DEDs).

We were able to measure experimentally the dissociation energy of *t*Bu-**1**₂. This was the necessary measure to validate computational methods which reveal the divided contributions of inter- or intramolecular interactions. In remarkable confluence of experiment and theory, we demonstrated that LD interactions between the *t*Bu groups are the decisive contribution counterbalancing the repulsive forces responsible for the spontaneous dissociation of HPE. Most importantly, we demonstrated the strength of these LD interactions with the all-*meta* *tert*-butyl triphenylmethane dimer, in which HPE's central C–C bond is formally substituted by a linear and extremely short C–H··H–C arrangement. Not only does the overall structure of *t*Bu-**1** survive, but the central C–H··H–C group is compressed to the shortest H··H contact reported to date (1.567 Å) – without any external help! Our spectroscopic investigations of a series of alkyl substituted triphenylmethyl derivatives excluded stereoelectronic substituent effects as a cause for the increased stability of *t*Bu-**1**₂.

*t*Bu-**1**₂ and Ad-**1**₂ are in equilibrium with their radical monomers in solution. Therefore, *t*Bu-**1**₂ and Ad-**1**₂ are thermodynamically more stable against dissociation than other R-**1**₂ species and it becomes evident that large, spherical and rigid substituents act as excellent DEDs,[99] even in solution. These hexaphenylethanes can be used as models for thermody-
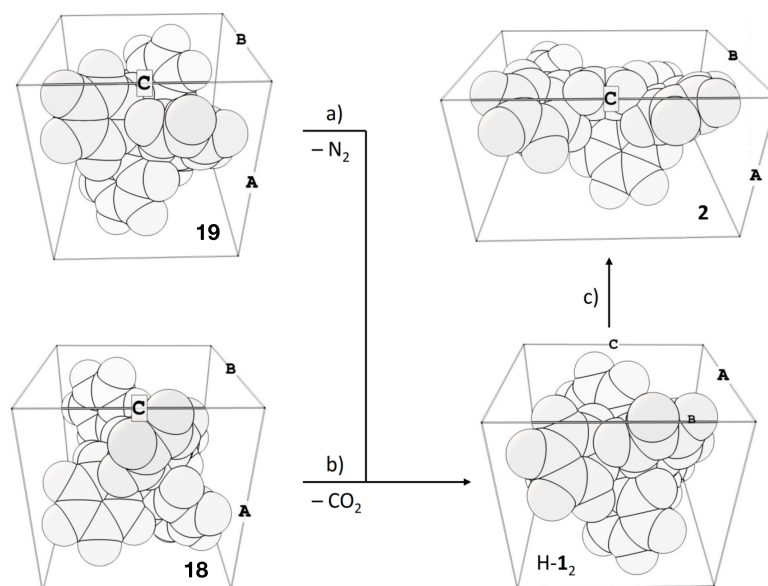
Figure 16. Comparison of the shape change during the extrusion of a) N_2 from 19 (Ph₃C−N=N−CPh₃) or b) CO_2 from 18 (Ph₃CC(O)OCPh₃) to yield H-1₂ and the rearrangement of the latter to 2.

namic LD stabilization and, in this regard, the obtained insights – the importance of size, fit, and rigidity to maximize the DED efficiency to stabilize peculiar structures – might be transferred to other fields like inorganic coordination chemistry,[132] supermolecular chemistry,[133] and synthetic organic chemistry, in particular, catalysis.[134]

The HPE story reveals the importance of synergy between experiment and theory: While Gomberg trusted his experiments more than the best available theory at the time, the reverse is true for Mislow who eventually trusted multiple computations more than the experimental results, thereby prompting a re-determination of a critical X-ray structure. Finally, experiment and theory agreed.

Subsequently, Grimme and Schreiner proposed on the basis of dispersion-corrected DFT computations that the bulky substituents in ^{t}Bu-$\mathbf{1_2}$ are responsible for its stability through mutual LD attraction. This gave birth to the concept of dispersion energy donors (DEDs) that are now increasingly used as strategic design elements in catalytic processes (*vide supra*). It is only a question of (long?) time until textbooks will also begin to appreciate a quantum-chemical based viewpoint on effects that are absolutely essential for understanding structures and chemical reactivities.

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