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J. Am. Chem. Soc., Just Accepted Manuscript • DOI: 10.1021/jacs.8b09145 • Publication Date (Web): 05 Oct 2018

Downloaded from http://pubs.acs.org on October 5, 2018

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Probing the Delicate Balance Between Pauli Repulsion and London Dispersion with Triphenylmethyl Derivatives

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Supporting Information Placeholder

ABSTRACT: The long known, ubiquitously present and always attractive London Dispersion (LD) interaction was probed with hexaphenylethane (HPE) derivatives. A series of all-meta hydrocarbyl [Me, ⁱPr, ^tBu, Cy, Ph, 1-Adamantyl (Ad)] substituted triphenylmethyl (TPM) derivatives [TPM-H, TPM-OH, (TPM-O₂, TPM[•]] was synthesized en route and several derivatives were characterized by single crystal X-ray diffraction (SC-XRD). Multiple dimeric head-to-head SC-XRD structures feature the excellent geometric fit between the meta-substituents; this is particularly true for the sterically most demanding ^tBu and Ad substituents. NMR spectra of the ^{*i*}Pr-, ^{*t*}Bu-, and Cy-derived trityl radicals were obtained and reveal, together with EPR and UV-Vis spectroscopic data, that the effects of all-meta alkyl substitution on the electronic properties of the trityl scaffold are marginal. Therefore, we concluded that the most important factor for HPE stability arises from LD interactions. Beyond all-meta ^tBu-HPE we also identified the hitherto unreported all-meta Ad-HPE. Intricate mathematical analysis of the temperature dependent dissociation constants allowed us to extract $\Delta G_d^{298}(exptl.) =$ 0.3(5) kcal mol⁻¹ from NMR experiments for all-meta ^tBu-HPE, in good agreement with previous experimental values and B3LYP-D3(BJ)/def2-TZVPP(C-PCM) computations. These computations show a stabilizing trend with substituent size in line with all-meta Ad-HPE ($\Delta G_d^{298}(exptl.) = 2.1(6)$ kcal mol⁻ ¹) being more stable than its ^tBu congener. That is, large, rigid, and symmetric hydrocarbon moieties act as excellent dispersion energy donors (DEDs). Provided a good geometrical fit, they are able to stabilize labile molecules such as HPE via strong intramolecular LD interactions - even in solution.

London Dispersion (LD) formally describes the attractive part of the van-der-Waals (vdW) potential and was first established by Fritz London to rationalize the condensation of noble gases.¹ LD was discovered as an important design element in chemistry quite a while ago,² but has only recently been appreciated in full.³ While LD is most apparent for nonpolar substances (e.g., hydrocarbons) it is ubiquitous and not related to a particular functional group.⁴ It also does not disappear in solution,⁵ not even in highly polar ionic liquids⁶ or in dimers of equally charged species.⁷ The important role LD plays for large biomolecules has been well established over the last decades.⁸

The unfortunate but widespread neglect of LD in chemical reasoning, in particular, in connection with steric effects, ^{3b, 3l} arises from the fact that LD interactions are considered small and often negligible. While it is true that a single individual LD interaction indeed is small, the strong gain in count of these pairwise additive interactions make LD interactions grow rapidly for increasingly larger molecules. Hence, the notion of LD overall being "weak" is not very meaningful in realistic chemical systems. Still, this notion supported the long standing oversight (despite better knowledge) that many practical implementations of density functional theory (DFT) did not include LD. Interpretable results were still acquired but they are likely due to favorable error compensation through the use of small basis sets and noninclusion of basis set superposition errors (BSSE) as well as solvation.9 This error compensation surfaced when DFT results were systematically compared with experiment and explicitly correlated methods that now have became available for increasingly larger molecular systems.¹⁰

Introduction



Figure 1. Representative hvdrocarbons 2-(1diamantyl)[121]-tetramantane 2a, bis(1-diamantyl) 2b and all-meta tert-butyl hexaphenylethane ^tBu- $\mathbf{1}_2$ with very long central C-C bonds prepared owing to large stabilizing LD interaction that outweigh Pauli exchange "steric" repulsion.^{3d,} 11

Some striking examples from our own work are represented through the remarkable structures of diamondoid¹² dimers, of which the [121]tetramantane-diamantane adduct 2a displays the longest C–C bond (1.71 Å) reported for an alkane to date (Figure 1); still, 2a is remarkably stable with an m.p. of 246 °C.^{3d, 11} A computational analysis [B3LYP-D/6-31G(d,p)] of the bond dissociation energy of the smaller congener bis(1-diamantyl) 2b showed that more than one third of its $\Delta G_d^{298} = 71$ kcal mol⁻¹ arises from LD. Similarly, all-meta tertbutyl hexaphenylethane ${}^{t}Bu-\mathbf{1}_{2}$ -one of the two isolable unbridged hexaphenylethanes prepared to date- displays a very long C–C bond (1.67(3) Å).¹³ TPSS-D3/TZVPP computations demonstrate that 62 kcal mol⁻¹ of the bond dissociation energy ($D_e = 34$ kcal mol⁻¹) are associated with LD interactions (the difference being other effects including Pauli repulsion).¹³ LD therefore is the decisive contribution to rationalize the unexpected stabilities of these hydrocarbons.

Quantifying LD is rather challenging as it is often associated 33 with, e.g., the hydrophobic effect¹⁴ so that it is difficult to 34 separate LD from other attractive forces.¹⁵ This is evident in 35 test systems originating from protein structures,^{8b, 16} 36 37 supramolecular entities¹⁷ or molecular balances including heteroatoms that lead to significant polar effects.5e, 18 38 Differential thermodynamic methods like the double mutant 39 cycle¹⁹ allow the observation of the interactions between 40 certain parts of the test systems. 41

42 Recently we proposed that all-meta alkyl substituted 43 hexaphenylethane [HPE; R-1₂; R = Me, ⁱPr, ^tBu, Cy, Ph, 1-44 Adamantyl (Ad)] derivatives are suitable testing systems for 45 determining the relative effects of dispersion energy donors 46 (DEDs²⁰).²¹ These molecules are pure hydrocarbons that may 47 form a weak covalent central C-C-bond in equilibrium with 48 their triphenylmethyl-type (trityl) radical monomers. Hence, 49 the equilibrium position reveals some information about the 50 DED ability of the interacting peripheral groups. Here, we 51 report the synthesis of the corresponding all-meta 52 triphenylmethyl chloride precursors, substituted the 53 properties of the corresponding radicals, and the challenges 54 associated with capturing the hexaphenylethane derivatives 55 in their equilibria with their radical monomers.

Results and discussion

The general approach (Figure 2 top) for the preparation of triphenylmethyl radicals (R-1) starts from 3,5-dialkyl-1halobenzenes (R-2), for which there are multiple synthetic routes. The corresponding organometallic species, typically Grignard or lithium reagents, add to a suitable C1-synthon, e.g., diethyl carbonate to give trityl alcohols (R-3). Their chlorination with acetyl chloride yields the corresponding halides (R-4). The radicals can then be generated via a single electron reduction using metals such as silver or zinc.

3,5-Dimethyl-1-bromobenzene (Me-2) is commercially available and 3,5-di-iso-propyl-1-bromobenzene (ⁱPr-2) is readily accessible starting from commercially available 2,6-diiso-proplyaniline via bromination, diazotation, and reduction.²² Triple Friedel-Crafts alkylation of tert-butyl chloride with AlCl₃ of benzene and subsequent mono-ipsobromination leads to 3,5-di-tert-butyl-1-bromobenzene (*Bu-2).²³ Similar approaches unfortunately do not work for the phenyl (Ph-2), cyclohexyl (Cy-2), and 1-adamantyl (Ad-2) derivatives. Ph-**2** was synthesized from 1,3,5tribromobenzene Br-5 with phenylboronic acid in a Suzuki C-C cross coupling reaction.²⁴ Cy-2 and Ad-2 were ultimately synthesized through Negishi C-C cross coupling (Figure 2 bottom).

Cyclohexyl zinc chloride 10 was generated via a Grignard reaction from cyclohexyl bromide 9 and subsequent transmetallation with zinc(II)chloride. The coupling to 1,3dibromo-5-chlorobenzene (Cl-5) with 2:1 mol-% ratio of 2dicyclohexylphosphino-2',6'-dimethoxybiphenyl

r.t. (SPhos²⁵)/Pd(OAc)₂ gave at 1-chloro-3.5dicyclohexylbenzene 11 in 96% yield. While cyclohexyl lithium is readily accessible²⁶ and cyclohexyl magnesium species are even commercially available, 1-adamantyl lithium²⁷ or 1-adamantyl magnesium species are very difficult to generate.²⁸ Fortunately, 1-adamantyl zinc chloride **13** is accessible in one step through an *in situ* Grignard reaction scavenged by zinc chloride stabilized with lithium chloride.²⁹ However, the coupling of 13 to CI-5 with 10:5 mol-% ratio of SPhos/Pd(OAc)₂ at 50 °C gave 3,5-di(1-adamantyl)-1chlorobenzene 15 only in up to 15% yield.

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Figure 2. Top: General approach for the preparation of allmeta alkyl substituted trityl radicals: a) Li⁰ or ^rBuLi or Mg, then (EtO)₂CO or Cl₂CO; b) SOCl₂ or AcCl; c) Ag⁰ or Zn⁰. Bottom: The synthesis of 3,5-dicyclohexyl-1-iodobenzene Cy-**2** and 3,5-di(1-adamantyl)-1-iodobenzene Ad-**2**. Conditions: a) Mg, THF, r.t., 60 min; then ZnCl₂, r.t., 10 min; b) cat. 2:1 SPhos/Pd(OAc)₂, Cl-**5**, THF, r.t., 3 h; c) Li⁰, cat. naphthalene, Et₂O, r.t.; then I₂, d) Mg, ZnCl₂, LiCl, THF, 2 h; e) cat. 2:1 SPhos/Pd(OAc)₂, TMS-5, THF, 50 °C, 3 h; f) I₂, AgCOOCF₃, MeOH, hexane, r.t., 1 h; g) 1. cat. 2:1 SPhos/Pd(OAc)₂, Cl-**5**, THF, 50 °C, 3 h, 15%; 2. Li⁰, cat. naphthalene, Et₂O, r.t.; then I₂, 7%.

Both 11 and 14 were rather difficult to metallate and only 40 41 lithiation of **11** using Li⁰ with catalytic amounts of 42 naphthalene in a broken glass/Et₂O slurry and subsequent 43 quenching of the 3,5-dicyclohexylphenyl lithium with iodine gave 3,5-dicyclohexyl-1-iodobenzene Cy-2 in 72% yield. 44 Treatment of 15 the same way to lithiate the strong C-Cl 45 46 bond facilitate solvolysis of the corresponding lithiated 47 species and mainly led to reduction. Only 7% of 3,5-di(1adamantyl)-1-iodobenzene Ad-2 were obtained. A more 48 suitable precursor to 3,5-di(1-adamantyl)-1-iodobenzene 49 was found with 3,5-dibromo-1-trimethylsilylbenzene (TMS-50 5). The Negishi coupling of 13 to TMS-5 with a 10:5 mol-% 51 52 ratio of SPhos/Pd(OAc)₂ at 50 °C gave 57% yield of isolated 3,5-di(1-adamantyl)-5-TMS-benzene 14. The iodine 53 commonly is demasked with ICl within a few minutes.³⁰ 54 Unfortunately, ICl reacts with adamantane under these 55 conditions,³¹ and I₂ together with AgCOOCF₃ as Lewis acid at 56

25 °C was used instead, yielding 95% of the product within 5 min. $^{\rm 32}$

The difficulties in the coupling of 1-adamantyl to the *meta* positions of the 1,3,5-substituted tri- or dihalobenzenes can be rationalized by the increased steric bulk and electronrichness leading to a slow first transmetallation (TM).³³ As the oxidative addition (OA) in the case of the coupling of **10** or **13** to Cl-**5** consists of the same catalyst and substrate there should be no difference. The reductive elimination (RE) is enhanced by bulky and electron donating ligands.³⁴ As the steric demand and electron donating ability of adamantyl is larger than that of cyclohexyl, the coupling of the former should be faster. This contradicts the observed drop in yield and RE can thus be excluded as the rate limiting step.

While there are numerous studies on the individual OA and RE steps, there are only few mechanistic studies for the TM in Negishi couplings.^{33c, 35} Most likely a square-plane Pd²⁺ complex of the composition [(η^2 -SPhos)Pd(Ar)Br] forms after the OA, where the SPhos ligand can switch to an η^1 binding mode to enable TM.^{25, 36} Steric congestion only would slow TM and merely explains the high amount of reduced **13**.

Ultimately, the electronic propensities of the benzene substituents have been included to understand why only fully substituted products are obtained and why TMS substitution leads to much higher yield. Our initial attempts to improve the yield employed an amide to mask the halide functionality. Subsequent hydrolysis and Sandmeyer reaction should lead to Ad-2. Indeed, the synthesis of N-boc-3,5di(1-adamantyl)aniline 1737 showed an increased yield of 30%. An analysis of Hammett's meta values³⁸ indicates a correlation between the electron donating nature of the substituents on the aryl and the yields [c.f. supporting information (SI)]. Successive exchange of electron withdrawing bromine against electron donating 1-adamantyl during the reaction therefore eases the subsequent couplings cycles. Likewise, an initially installed electron donating group such as TMS leads to a faster overall reaction and improved yields.

Lithiation of Me-, ⁱPr-, ⁱBu-, Cy-, and Ph-**2** with ⁱBuLi at -78 °C proceeded smoothly. After addition of diethyl carbonate at 25 °C the corresponding trityl alcohols R-**3** were isolated in good to excellent yields [93% (Me); 85% (ⁱPr); 78% (ⁱBu); 94% (Cy); 71% (Ph)]. The synthesis of Ad-**3** was more delicate and initially failed under the common conditions. The major product was identified as 1,1'-di(3,5-di(1-adamantyl)phenyl)-1"-*tert*-butylmethanol and laborious to seperate. Performing the addition of ⁱBuLi in a titration like manner and avoiding any super- or substoichiometric addition of ⁱBuLi gave up to 64% yield.

Attempts to improve the synthesis of Ad-**3** by application of a Grignard species by metal-halogen exchange would require at least 2.2 equiv. ⁱPrMgCl·LiCl at 0 °C for full conversion of Ad-**2**. However, excess of ⁱPrMgCl·LiCl solely led to the *iso*propylated compound. Grignard reaction of ⁱBu- or Ad-**2** with Mg-powder were initiated by substoichiometric amounts of ⁱPr-MgCl·LiCl or DiBAL–H and gave good conversion to the Grignard species. Unfortunately, treatment of these with diethyl carbonate or phosgene did not yield Ad-**3** and ^tBu-**3** in only 20%.



Figure 3. Halogenation procedures for R-3.

Fundamental for the synthesis of the HPE derivatives $R-1_2$ or the radical monomers $R-1^{\bullet}$ is the synthesis of the corresponding all-*meta* alkyl triphenylmethyl halides. Chlorination of R-3 to all-*meta* alkyl triphenylmethyl chlorides (R-4) with acetyl chloride worked similarly well for the alkyl derivatives [61% (Me); 59% (ⁱPr); 84% (ⁱBu); 69% (Cy); 55% (Ad)]. Chlorination of Ph-**3** was cumbersome and Ph-**4** was resistant to single electron transfer (SET) from Zn(Cu) or Ag. The treatment of Ph-**3** with HBr/AcOH gave the corresponding bromide Ph-**18** in 71% yield (Figure 3). The same reaction with ⁱPr-**3** gave 64% yield of ⁱPr-**18** but the obtained colorless crystals rapidly cracked and turned brown even under exclusion of moisture and light at -20 °C. This illustrates the sensitivity of the alkyl derivatives R-**18** and consequently only R-**4** was used further.

Precursors and Related Species

The generation of R-1[•] sometimes also causes significant decomposition and side product formation (Figure 4). It was therefore necessary to prepare these to provide reference spectral data for the detailed interpretation of the spectra of the mixtures containing the radicals. Hence, the triphenylmethanol (R-3), triphenylmethane (R-19), and bis(triphenylmethyl)peroxide derivatives (R-20) as well as the triphenylmethyl carbocations R-21 were synthesized for proper spectral analyses.



Figure 4. Generation of R-**1**[•] and decomposition channels leading to hydrolysis (R-**3**), hydrogen abstraction (R-**19**), and oxidation (R-**20**) products. Chloride abstraction from R-**4** by zinc(II)chloride leads to carbocations R-**21**.

Hydrocarbons. Hydrocarbons R-**19** were synthesized by treatment of R-**3** with NaBH₄/AlCl₃.³⁹ The single crystal X-ray diffraction (SC-XRD) structure of 'Bu-**19** reveals a head-to-head arrangement of two independent molecules.^{3w} The neutron diffraction (NRD) structure displayed the shortest *inter*molecular C-H···H-C contact ($R_{H\cdot··H} = 1.566(5)$ Å) reported to date; for a very short *intra*molecular contact see ref.⁴⁰ The underlying interaction enabling this short $R_{H\cdot··H}$ was found to be largely LD. The C-H···H-C contact in 'Bu-**19** is arranged in a straight line [γ (C-H···C') = 180°] with an angle between their C_{ipso}C'_{ipso}C''_{ipso} planes (P_C) θ (P_C;P'_C) of 0°. The phenyl rings around the central carbons are arranged in a propeller-like fashion (Π -rotamer in Figure 5a).

Similar head-to-head arrangements were found in the SC-XRD structures of Me-**19** ($P\overline{1}$) and the two crystal modifications found for Cy-**19** ($P\overline{1}$ and $P2_1/c$). In these arrangements the C–H···H–C contacts are shifted. As observed for 'Bu-**19**₂ the $R_{H-\cdot\cdotH}$ of Me-**19** and Cy-**19** are distinctly below the sum of their vdW radii. In line with the DED concept the $R_{H-\cdot\cdotH}$ distance is 2.08 Å for the smaller and less effective methyl group DED in Me-**19**^{3w} while it is reduced to 1.83 Å for the larger Cy-**19**. The latter is 25% shorter than expected from the sum of the vdW radii even when the R_{C-H} distance is fixed to 1.00 Å (as customary for X-ray structure determination). Not unexpectedly, this makes cyclohexyl a much better DED than a methyl group on the basis of their sizes and polarizabilities.

The phenyl rings in the first independent molecule in the asymmetric unit of Cy-**19** in $P\overline{1}$ form a propeller like (Π) arrangement akin to ^tBu-**19** (Figure 5b). The flatter structure of the Cy substituents in comparison to ^tBu allows for a parallel shift of the C–H bonds by 0.70 Å to avoid in part the repulsive interaction through the short H…H contact. The phenyl rings in the second independent molecule are arranged like rabbit-ears (B) (Figure 5c) and the C–H bonds are significantly shifted (3.54 Å). The second modification found for Cy-**19** ($P2_1/c$) consists of a mixed B/ Π dimer. Here,

repulsion is reduced through an angled arrangement $(\theta(P_C;P'_C) = 35.9^\circ, R_{H\cdots H} = 2.37 \text{ Å}; Figure 5d).$

Both arrangements found in Me-**19** consist of a parallel shifted B·B dimer. The tight dimer still contains a 13% shorter $R_{\text{H} \rightarrow \text{H}}$ than the sum of the vdW radii; the C–H bonds are shifted by 0.68 Å. The second dimer is stronger shifted and therefore has a $R_{\text{H} \rightarrow \text{H}}$ of 2.55 Å. Parent H-**19**⁴¹ and ⁱPr-**19** show no such arrangement. Both crystallize as Π -rotamers. The latter prefers an in-line head-to-tail arrangement (*cf.* SI).



Figure 5. a) The two observed rotamers for R-19. Depicted are the dimers for Cy-19 formed by b) the pure Π-form in P1, c) the pure B-form in P1, and c) the mixed Π·B dimer in P21/c. Disorders, cyclohexyl groups and non-methyl hydrogens are omitted for clarity. Ellipsoids are drawn at 50% probability.

Alcohols and Chlorides. Alcohols R-3 and chlorides R-4 were synthesized as described above. Common alcohols form bond networks in the solid state.42 hydrogen Triphenylmethanol forms a dynamic tetrameric hydrogen bond bonding arrangement⁴³ resulting in a broad infrared (IR) signal at 3472 cm^{-1.44} The all-meta substituted trityl alcohol derivatives R-3 instead form no hydrogen bond networks. The attenuated total reflection (ATR)-IR spectra of the R-3 derivatives feature a sharp O–H stretching vibration in the range of $v(O-H) = 3550-3610 \text{ cm}^{-1}$ (Figure 7). These arise from stretching vibrations of isolated hydroxyl functions. Monomeric MeOH absorbs at 3664 cm⁻¹, dimeric MeOH show a band splitting that is about 150 cm⁻¹ redshifted for the hydrogen bond donor.⁴⁵ ^tBu- and Cy-**3** also show red shifts with broad bands at 3428 and 3413 cm⁻¹, respectively, indicating hydrogen bridged dimers. The IR spectra are in line with the corresponding SC-XRD structures. Me-**3** crystallizes in space group $P2_1/c$ (c.f. SI) and shows only one type of isolated OH functions according to one sharp ν (O–H) of 3601 cm⁻¹. The SC-XRD structure of ^tBu-**3** ($P2_1/n_i$) Figure 6a) instead reveals two independent molecules of

^rBu-**3** in the asymmetric unit. Here the hydrogen of one OH function is located between the two oxygen atoms [γ (O^D– H···O^A) = 178.1°], the other hydrogen is uncoordinated. Both molecules have common geometrical features and form an angled arrangement [θ (P_C;P'_C) = 28.5°]. A similar arrangement is found for Cy-**3** [Figure 6b; $P2_1/c$; R = 0.104; θ (P_C;P'_C) ≈ 29°], but the severe whole molecule disorder of this SC-XRD structure prohibit an exact analysis.



Figure 6. The asymmetric units of the SC-XRD structures of a) ^tBu-**3** and b) Cy-**3** consist of two independent molecules. Some *tert*-butyl groups in (^tBu-**3**)₂ show disorder. (Cy-**3**)₂ also is disordered and the depicted structure has an occupancy of >48%. Disorders, non-hydroxyl hydrogens and alky groups were omitted for clarity. Ellipsoids are drawn at 50% probability.



Figure 7. Details of the ATR-IR spectra of the R-**3** derivatives. The marked absorption bands correspond to the ν (O–H), free (sharp) or involved in hydrogen bonding (lower wavenumbers, broad).

SC-XRD structures of the halogenated derivatives were obtained for ⁱPr-**18**, ⁱPr-**4**, and Ad-**4** (c.f. SI). These crystallize as non-dimeric Π -rotamers with common geometrical features. ⁱPr-**18** and ⁱPr-**4** show the same disorder at some ⁱPr groups. The Ad-**4** structure has C_3 symmetry axis along the C–Cl bond and displays a similar disorder in all Ad groups. The disorder arises by twisting the adamantyl groups about 60° around the C_{meta}-C_{α} axis. All R-**4** derivatives show a characteristic downfield chemical shift of the halogenated versus the hydroxylated methyl carbon (Table 1). The narrow chemical shift range of the central carbon in the series of alcohols and chlorides reveals a negligible electronic effect, in accordance with the very small changes in linear freeenergy relationship parameters for induction or resonance.^{38b}

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Table 1. ¹³C-NMR shifts of the substituted methyl carbon in different all-*meta* substituted trityl derivatives. Chemical shifts δ measured in C₆D₆, given in ppm relative to the solvent peak.

(3,5- R ₂Ph)₃ C - X	ОН	CI	00	н	R ^{⊕ c)}	R ₂
Me	82.3	83.0		57.5		
ⁱ Pr	83.1	83.6	94.2	58.2		
Су	83.2	84.1	94.3	58.3		
					210.	71.5
^t Bu	83.7	84.4	95.3	58.7	1	b)
1-Ad	84.0	85.2		59.5		
	82.9	82.4	94.5	58.1		
Ph		79.3 ^{a)}				

^{a)}Chemical shift of the bromide. ^{b)}Measured in C₆D₁₂. Literature value 70.7 ppm.⁴⁶ ^{c)} δ (Trityl cation · TfO in CD₂Cl₂) = 211.4 ppm.⁴⁷

Peroxides. The peroxides R-20 were obtained through the reaction of oxygen with R-1[•] typically giving poorly soluble materials. Filtration and recrystallization yielded pure R-20. However, attempts to synthesize Me-20 *via* this route gave a complex, inseparable mixture. The synthesis of Me-20 was not pursued further as it did not form under the reaction conditions of Me-1₂ synthesis. SC-XRD structures were obtained for ⁱPr-20, Cy-20·Et₂O, Ad-20·4(C₆H₆), and Ph-20. The SC-XRD structures of H-20⁴⁸ and ^tBu-20⁴⁹ are literature known.

The peroxides do not appear particularly strained, neither between the trityl moieties nor their substituents. The torsion angles $\tau(C_{methy}|-O-O'-C'_{methy}|)$ for R-**20** were 180° throughout and only unsymmetric Π -rotamers were found. The shapes of the peroxide substructures were very similar within this series: $R_{C-O} = 1.456(+5/-6)$ Å, $R_{O-O} = 1.476(+6/-7)$ Å, $\gamma(C_{methy}|-$ O-O') = 107.7(+1.1/-0.4)°; the trityl moieties are very similar. The averaged $\gamma(C_i-C_{methy}|-C_i')$ is $112.4(\pm 4)$ ° and deviations from this value with increasing substituent size are randomly scattered. Still, the substituents most aptly gear into each other in Ad-**20** allowing multiple attractive interactions (Figure 8). Some of these interactions are lost in Cy-**20** due to the flatter structure of the Cy substituents. Lastly, the numerous geometrical constrains in Ph-**20** allow only for one angled, Tshaped or one parallel-shifted intramolecular contact. These features agree well with the computational trends found for R-**1**₂.²¹



Figure 8. Comparison of the molecular structures (SC-XRD) of Ad-, Cy-, and Ph-**20**. Right column: close-ups of the equivalent representations of the noncovalent interaction (NCI) plots⁵⁰ of one substituent on top of the opposing phenyl ring buried within surrounding substituents (s = 0.5 au/-0.04 < ρ < +0.04 au). Solvent molecules, disorders, and hydrogens were omitted for clarity.

The very different NMR and UV-Vis properties of the trityl cations (R-**21**) versus the neutrals allowed detailed NMR and UV-Vis spectral investigations of the 'Bu-**21** cation that is representative for the R-**21** cation series. The UV-Vis spectrum was recorded after treatment of 'Bu-**3** with MsOH in benzene and showed an absorption maximum at $\lambda_{max} = 431$ nm, in good agreement with time dependent (TD)-DFT at B3LYP-D3(BJ)/cc-pVDZ(conductor-like polarizable continuum model (C-PCM):Benzene) computations (414 nm, f = 0.47). The NMR spectrum of 'Bu-**21** was obtained after reacting 'Bu-**3** with HBF₄, TfOH or MsOH in C₆D₆. The aromatic hydrogens experience a severe downfield shift from 7.28/7.04 ppm for 'Bu-**3** to 8.27/7.56 ppm for 'Bu-**21**. The

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chemical shift of the ^tBu group was nearly unaffected. Similar shift effects were observed in the ¹³C NMR, thereby also indicating that *meta* substitution on the trityl moiety exerts little electronic influence. Consequently, treatment of ^tBu-4 with ZnCl₂ in C₆D₆ resulted in very similar UV-Vis spectra as found for ^tBu-**21** with λ_{max} around 433 nm. The ¹H-NMR of ^tBu-4 with ZnCl₂ gave two broadened peaks at 8.22 and 7.78 ppm in a 1:2 ratio. These likely arise from an equilibrium of t Bu-**4** with ZnCl₂ that acts as a weak Lewis acid.

Trityl Radical Derivatives

10 Radical generation was performed in benzene via SET from 11 Zn(Cu) to R-4 for the alkyl derivatives or to Ph-18. 12 Concentrations where kept at 22-27 mmol L⁻¹ for NMR and 13 ~5 mmol L⁻¹ for EPR experiments. The poor solubility of the 14 1-adamantyl derivatives limited the concentration to about 15 10 mmol L⁻¹. NMR spectroscopy of radicals is limited to ¹H 16 as the signal intensity of the other nuclei is already very low 17 and vanishes completely due to electron spin-core spin 18 coupling. Very broad signals were observed in case of ⁱPr-1. 19 (2.33 ppm), ^tBu-1[•] (1.83 ppm),²¹ and Cy-1[•] (0.75, 1.04 and 20 2.09 ppm) as shown in Figure 9. The three ¹H-NMR peaks in 21 Cy-1. have an approx. 5:2:3 ratio. The large amounts of 22 23 byproducts upon radical generation of Ad-1 and the generally broadened adamantyl ¹H-NMR signals prevented 24 the unambiguous identification of Ad-1 via NMR. While an 25 enhancement of the broadened signals for ^tBu-1[•] and Cy-1[•] 26 was observed in CD_2CI_2 (Figure 9), the reaction mixture 27 containing Ad-1 in CD₂Cl₂ showed no such effect. Neither 28 the samples of the methyl nor the phenyl derivative showed 29 broadened signals. Even paramagnetic ¹H-NMR 30 spectroscopy (-80 to 140 ppm; 0.1 s relaxation delay; 0.27 s 31 acquisition time) did not reveal signals that could be related 32 to these radicals (for the full spectra see SI). In all cases the 33 remaining major signals were identified as either R-3, R-19, 34 R-20, or R-21. We found no evidence for the formation of 35 van-der-Waals (R-1)₂ or covalent R- $\mathbf{1}_2$ dimers in benzene. 36



Figure 9. ¹H-NMR spectra of ⁱPr-1[•], ^tBu-1[•], and Cy-1[•] in C₆D₆ (black lines/blue dots) and CD₂Cl₂ (grey lines and dots).

An explanation for the invisibility of Ph-1 and in particular Me-1 was delivered by EPR spectroscopy and spin density (ρ_{soin}) computations. EPR spectra of all R-1[•] derivatives in benzene were recorded. ^tBu-1[•] yielded a well resolved EPR spectrum (Figure 10c). Despite equal concentrations and sample preparation none of the other spectra was equally well resolved. The EPR spectrum of ^tBu-**1** revealed mainly hyperfine splitting due to the ortho and para hydrogens (Figure 10c) in accordance with the literature.⁵¹ In ^tBu-**1**[•] no spin coupling with the tert-butyl hydrogens was observed but a ¹H NMR signal from the latter was visible. The EPR spectra of ⁱPr-1[•], ^tBu-1[•], Cy-1[•], and Ph-1[•] featured the same superordinate splitting pattern into ten peaks. Only the EPR spectrum of Me-1. in benzene is clearly different (Figure 10f). All α -methyl hydrogens in Me-1 couple strongly with the unpaired electron to give a complex multiplet. This is in line with the assumed significant spin density at the benzylic positions (Table 2) and explains the lack of NMR signals for Me-**1**•. ⁱPr-1[•] represents an intermediate species as it features additional subtle couplings to the six methine hydrogens. No coupling to the β -methyl hydrogens was observed and the NMR spectrum is indicative of a radical species. The large line width in the EPR spectra of Cy-1 and Ph-1 prevent a detailed analysis of their spin distributions.





Computations of the radicals at the B3LYP-D3(BJ)/cc-pVDZ level of theory are instructive (Table 2). The more remote the position of the hydrogens in the substituent regarding the trityl scaffold, the more likely it is to observe a ¹H-NMR signal (Figure 11). As a reminder, we observed ¹H NMR peaks for ⁱPr-1[•], ^tBu-1[•], and Cy-1[•] but not for Me-1[•] and Ph-1[•]. α -Alkyl hydrogens carry a $\rho_{spin} > 0.2 \text{ m}\mu_{B}/\text{Å}^{-3}$ and are not observable

via NMR; the α -hydrogens in Me-1[•] carry a seven times higher spin density than 'Pr-1[•] or Cy-1[•]. The aromatic π system in Ph-1[•] spreads the spin density over all hydrogens (>0.1 mµ_B/Å⁻³) and no ¹H-NMR signal is observed. Thus, spin densities lower than this value are necessary to observe ¹H-NMR signals. Similar to the small substitutent effect on the ¹³C NMR (Table 1) neither in the EPR ($\Delta \alpha_{max} = 0.06 \text{ G } [\pm 1\%]$) spectra nor the computed spin densities ($\Delta \rho_{spin} = 0.015 \mu_B \text{ Å}^{-3}$ [±2%]) show significant effects.

Table 2. Averaged, absolute magnitude of the computed natural bonding orbital analysis spin densities of the atoms at the corresponding positions at B3LYP-D3(BJ)/cc-pVDZ. Values in 1000 $\cdot \mu_B \text{ Å}^{-3}$. Values in italics are likely to be observed by ¹H-NMR.

Positio n	Ato m	Substituent					
		Me	ⁱ Pr	Су	^t Bu	Ad	Ph
			Trityl o	core			
central	С	556	561	547	551	531	555
р	Н	3.53	3.49	3.68	3.48	3.52	3.57
0	Н	3.63	3.48	3.52	3.50	3.79	3.58
	Substituent						
α	Н	1.34	0.18	0.21			
β	Н		0.01	0.05	0.01	0.02	0.18
γ	Н			0.02		0.04	0.10
δ	Н			0.00		0.01	0.20



Figure 11. Representation of the computed all-*meta* cyclohexyl trityl radical [B3LYP-D3(BJ)/cc-pVDZ] carbon atom spin densities colored in blue (the more intense color indicates higher spin density). Hydrogens are omitted for clarity.

The benzene solutions containing Me-, 'Pr-, 'Bu-, Cy-, and Ad- **1**• appear orange, while the solution containing Ph-**1**• is red. UV-Vis spectra of the reaction mixtures containing alkyl R-**1**• show an absorption around 433 nm (Figure 12). The UV-Vis spectrum of the reaction mixture of 'Bu-**1**• matches with the

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spectrum of the corresponding cation. Nonetheless, cationic R-**21** was observed *via* NMR only in case of the reaction mixture containing Ad-**1**[•]. The color of the R-**1**[•] reaction mixtures must therefore emerge from very low concentrations of R-**21**. The small change in λ_{max} over the series of alkyl derivatives in comparison to the parent H-**21** (λ_{max} = 432 nm) emphasize the negligible influence of alkyl substitution on the electronic properties of the trityl scaffold.⁵²

Time dependent (TD)-B3LYP-D3(BJ)/cc-pVDZ (C-PCM:benzene) computations of ^tBu-1[•] give the main absorption at 361 nm (f = 0.29). This is 52 nm blue-shifted as compared to the most intense absorption of ^tBu-21 that is about twice as strong. Longer reaction times in low concentration reaction mixtures of ^tBu-4 with Zn(Cu) in benzene showed a UV-Vis spectrum with a λ_{max} = 352 nm in good agreement with the computed TD-spectrum of ^tBu-1[•]. This is also in line with experimental and computational UV-Vis spectrum of the unsubstituted trityl radical ($\lambda_{max} = 338$ -340 nm).⁵³ Other uncharged closed-shell trityl derivatives absorb close to or below the absorption edge of benzene (e.g., the Jacobsen-Nauta structure: $\lambda_{max} = 315 \text{ nm}^{54}$) and do not contribute to the UV-Vis spectra in benzene.



Figure 12. UV-Vis spectra of the reaction mixtures containing R-**1**[•] in benzene. $\lambda_{max} = 435$ (Me); 434 (ⁱPr); 438 (Cy); 432 (ⁱBu); 440 (Ad); 504, 371 (Ph) nm.

Hexaphenylethane Derivatives

The SET to ^tBu-**4** in cyclohexane-d₁₂ also produced a bright orange solution; the reaction is slower than in benzene.²¹ A ¹H NMR spectrum of this solution featured the radical signals as well as a set of five new peaks. These could be assigned to all-*meta tert*-butyl hexaphenylethane Bu-**1**₂. A variable temperature (VT)-NMR/van 't Hoff analysis revealed a dissociation energy of ΔG_d^{298} (exp.) = -1.6 kcal mol⁻¹, in good agreement with theoretical predictions.¹³

Subsequent computations predicted increasing stability in the series of R-**1**₂ due to increasing LD,²¹ but these computations quantitatively differ from experiment as they neither take the equilibrium with a vdW dimer¹³ (R-**1**·)₂ nor the Jacobsen-Nauta-structure (R-**22**; Figure 13a) into account.^{54a, 55} An improved computational analysis was performed here at B3LYP-D3(BJ)/def2-TZVPP(C- PCM:CyH)//B3LYP-D3(BJ)/cc-pVDZ(C-PCM:CyH) to reduce the BSSE and to allow a more precise assessment of the relative stabilities of R-**1**₂, (R-**1**[•])₂, and R-**22** (Table 3, Figure 13b). These results agree with experiment for the free dissociation energy of ^tBu-**1**₂ within 0.2 kcal mol⁻¹. Previously LD was estimated by comparison of the dispersion corrected with the uncorrected DFT computations [$E_{disp} = D_e(B3LYP-$ D3(BJ))– $D_e(B3LYP)$]. The alternative way employed here is the reduction of LD upon dissociation, obtained as $E_{disp} =$ $2 \cdot D3(BJ)[R-$ **1**[•]] – D3(BJ)[R-**1**₂]. The magnitude of the D3(BJ)dispersion correction depends on the functional. The D3(BJ)values utilizing the B3LYP functional combination compare $reasonably well to more rigorously defined <math>E_{disp}$, e.g., from symmetry adapted perturbation theory (SAPT).

These computations show that R-22 contributes only in the case of the parent triphenylmethyl H-22. Substitution with Me leads to an overall destabilization in favor of free Me-1. Further increase in bulkyness renders ⁱPr-**1**₂ and ^tBu-**1**₂ almost isoenergetic with their monomers R-1[•]. $\Delta G_d^{298}[(^tBu-1^{•})_2 \rightarrow$ ^tBu- $\mathbf{1}_2$] is -1.8 kcal mol⁻¹, in perfect agreement with previous experiments. $R-\mathbf{1}_2$ is stabilized by substitution with the larger Cy group, for which $Cy-\mathbf{1}_2$ is the most stable form: $\Delta G_d^{298}[(1)_2 \rightarrow 1_2] = 1.5 \text{ kcal mol}^{-1}$. Ultimately, Ad- 1_2 is 11.8 kcal mol⁻¹ [$\Delta G_d^{298}[(\mathbf{1})_2 \rightarrow \mathbf{1}_2]$ more stable than any other arrangement. As $(Ad-1)_2$ displays no symmetry, we were unable to compute vibrational frequencies at a meaningful level of theory and its ΔG_d^{298} was therefore estimated from the single point energy of $(Ad-1)_2$ and the ΔG correction from Ad- $\mathbf{1}_2$. (Ph- $\mathbf{1}$)₂ should solely exist as a single species in the reaction mixture. $R-1^{\bullet}$ and $(R-1^{\bullet})_2$ are indistinguishable via NMR but it is plausible to assume based on the computational analysis solely an equilibrium between R-12 and the energetically next lowest species, which is R-1° for Me and ⁱPr and (R-1)₂ for all other derivatives.

Table 3. Computed ΔG_d^{298} and E_{disp} values for the dissociation of all-*meta* substituted trityl radical complexes (R-1[•])₂, hexaphenylethanes R-1₂ and Jacobsen-Nauta structures R-22 at the B3LYP-D3(BJ)/def2-TZVPP(C-PCM:CyH)//B3LYP-D3(BJ)/ cc-pVDZ(C-PCM:CyH) level of theory. All energies in kcal mol⁻¹.

	α ^{a)}	(R- 1 •) ₂		R- 1 ₂		R- 22	
R =	[ų]	ΔG_{d}^{298}	E _{dis} р	ΔG_d^{29}	E _{disp}	ΔG_d^{298}	E _{disp}
Н	0.8	0.9	25. 4	-12.6	32.2	_ 10.0 ^{b)}	16.8
Me	2.6	-1.1	37. 5	-14.1	42.7	-20.1	29.4
ⁱ Pr	6.2	-5.2	54. 7	0.5	64.4	-27.7	52.1
^t Bu	8.0	4.3	42. 7	2.5	70.9	-25.5	60.9
Су	10. 8	14.9	67. 2	16.4	87.0	-4.3	65.4

Ph	10. 0	25.6	96. 0	6.9	108. 6	-4.0	72.3
Ad	15. 9	16.6 ^c	96. 3	28.4	114. 8	5.0	105. 5

^{a)}Isotropic polarizability of the corresponding hydrogen capped substituent R-H.⁵⁶ ^{b)}The exptl. $\Delta G_d^{298} = 4.7$ kcal mol⁻¹ determined via EPR is presumably too positive due to uncertainties through invisibility of closed-shell decomposition products.⁵⁷ c⁾ ΔG_d^{298} was calculated from the single point energy of (Ad-1[•])₂ and the ΔG correction from Ad-1₂.



Figure 13. a) Relations between R-1₂, (R-1[•])₂, R-1[•], and R-22. b) Computed free dissociation energies ΔG_d^{298} at B3LYP-D3(BJ)/def2-TZVPP(C-PCM:CyH)//B3LYP-D3(BJ)/cc-pVDZ(C-PCM:CyH) of (R-1[•])₂, R-1₂, and R-22 relative to 2 R-1[•]. The circle diameter correlate with E_{disp} .

Due to the unpredictability of solvent effects and the many challenges associated with solubility of our substrates and their dissociation products, we decided to investigate the already available radicals in cyclohexane. The reaction mixtures containing ⁱPr-, ^tBu-, Cy-, and Ad-**1**[•] were orange and became increasingly cloudy with increasing molecular weight; after filtration clear solutions were obtained. The intensity of the orange color of these solutions decreased with molecular weight until an almost colorless solution was obtained for Ad-**1**[•]. This color trend is indicative (although not necessarily connected) of the decrease of signal intensity of the radicals R-**1**[•] in NMR – from a strong signal for ⁱPr-**1**[•] to no signal for Ad-**1**[•].

For Ad-**1**[•] we were able to assign three aromatic signals at 7.67, 7.09, and 5.95 ppm in the ¹H NMR spectrum to Ad-**1**₂. The chemical shifts agree well with gauge-independent atomic orbital (GIAO) B3LYP/6-31G(d,p)(C-PCM:CyH) computations (Table 4). The offset between computational and experimental chemical shifts is very similar to the offset for ^tBu-**1**₂.²¹ The three triplets (⁴J = 1.7 Hz) have a 1:1:1 ratio,

share one spin system according to correlation spectroscopy (COSY) NMR experiments, and their intensities show a strong, reversible temperature dependency (Figure 14). The solubility of all all-*meta* 1-adamantyl trityl derivatives in C₆D₁₂ is very low. It was therefore only possible to record ¹H NMR spectra of the reaction mixture of Ad-**1**₂ in C₆D₁₂. Other solvents like CD₂Cl₂ or toluene-d₈ did not show similar peaks even at temperatures as low as -65 °C.



Figure 14. ¹H VT-NMR of a) ^tBu- $\mathbf{1}_2$ and b) Ad- $\mathbf{1}_2$ featuring three unique signals for the three nonequivalent, aromatic hydrogens as described for ^tBu- $\mathbf{1}_2$.²¹

Table 4. ¹H-NMR chemical shifts in C_6D_{12} from experimental and computed spectra for ^tBu- and Ad-1₂. Chemical shifts were computed with GIAO B3LYP/6-31G(d,p)(C-PCM:CyH) and were averaged per position. Values of ^tBu-1₂ are taken from²¹.

H-position:		0 _{in}	р	0 _{out}	R _{in}	R_{out}
exp. ^t Bu- 1 ₂ com p.	7.7 5	7.1 9	6.0 2	0.98	0.95	
	com p.	8.1 7	7.5 3	6.2 6	1.07	1.01
$Ad\text{-}1_2$	exp.	7.6 6	7.0 9	5.9 5	n. a.	n. a.

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com	7.9	7.5	6.0	0.98-	0.97–
p.	9	5	1	2.24	2.23

The obscured NMR signals of Ad-**1** prevent the direct use of a van 't Hoff plot. Based on the law of mass action, the law of mass conservation, and the strict proportionality between concentration and NMR signal intensity we established a mathematical solution (for the deviation see SI) solely based on the temperature dependency of the NMR signal intensity I_{12} of R-**1**₂:

$$I_{1_2}(T) = I_0 \left[1 + \frac{e^{-a_{/T}}}{8B_0} \left(1 - \sqrt{1 + 16B_0 e^{a_{/T}}} \right) \right]$$
(1)

with I_0 being the signal intensity at T = 0 K, $B_0 = K_0/C_0$ the equilibrium constant K_0 at T = 0 K scaled by the initial concentration C_0 of R-**1**₂, and $\boldsymbol{a} = \Delta H_d^{298}/R$, the enthalpy of dissociation and the ideal gas constant R. A multi-parameter fit to the recorded VT-NMR data directly provide I_0 and ΔH_d^{298} . ΔS_d^{298} is then indirectly accessible *via* the van 't Hoff plot and gives access to the free dissociation energy *via* $\Delta G_d^{298} = \Delta H_d^{298} - T\Delta S_d^{298}$.

As a validation, fitting of the 'Bu-**1**₂ VT-NMR intensities of the equilibrium between 'Bu-**1**₂ and Bu-**1**[•] to equation (1) yields $\Delta H_d^{298} = 9.2(4)$ kcal mol⁻¹, only 1.3 kcal mol⁻¹ higher than determined *via* the classic van 't Hoff approach.²¹ The *a posteriori* application of the van 't Hoff plot with the observed I_0 reveal $\Delta S_d^{298} = 30.0(3)$ cal mol⁻¹ K⁻¹. In sum a ΔG_d^{298} of 0.3(5) kcal mol⁻¹ is obtained that is well in line with previous findings.

30 Processing of the Ad-1₂ VT-NMR intensities in the same 31 manner gives $\Delta H_d^{298} = 10.5(5)$ kcal mol⁻¹. Together with 32 $\Delta S_d^{298} = 28.3(3)$ cal mol⁻¹ K⁻¹ from the van't Hoff treatment. 33 That is, this HPE derivative is slightly more stable with ΔG_d^{298} 34 = 2.1(6) kcal mol⁻¹, in qualitative agreement with our earlier 35 theoretical predictions.²¹ The strong, reversible temperature 36 dependence of the NMR intensities is unexpected as $Ad-\mathbf{1}_2$ 37 should not take part in an observable equilibrium with Ad-1. 38 according to the computed ΔG_d^{298} , which is about a 39 magnitude higher than the experimental value. 40

For ⁱPr- and Cy-1 · variable temperature NMR was unrevealing 41 as the concentrations of these species apparently are too low 42 to be observable via NMR. This threshold is estimated as a 43 $R-1^{\bullet}/R-1_2$ ratio higher than 99.9:0.01 which corresponds to 44 $c(R-1_2) < 0.025 \text{ mmol } L^{-1}$. These derivatives therefore have a 45 ΔG_d^{298} below –4.5 kcal mol⁻¹. The 12-fold interactions 46 between the substituents amplify the pairwise effect and 47 ΔG_d^{298} cause а steep increase in with 48 polarizability/substituent size that readily transcend the 49 narrow energy regime where an equilibrium can be observed. 50 Only ^tBu- and Ad- $\mathbf{1}_2$ are stabilized enough through their 51 substituents to be observable. It is therefore evident that 52 53 rigid and spherical ^tBu and 1-Ad involve significantly stronger dispersion interactions in solution than flexible and flat ⁱPr or 54 Cy. This contradicts our computations where both ⁱPr-, ^tBu-, 55 and Cy - $\mathbf{1}_2$ similarly have a ΔG_d^{298} of about 0 kcal mol⁻¹ but 56 Ad- $\mathbf{1}_2$ is more stable by one order of magnitude. 57

R-**1**₂ was not observable in any solvent other than cyclohexane. This demonstrates the large influence of the solvent on the stability of these compounds.⁵⁹ The solvent influence is acceptably described by C-PCM for the effect of non polar solvents on the electronic energy but poorly for the entropy. On top, there are multiple conformers found within 1 kcal mol⁻¹ by force field conformer searches for R-**1**₂. These could not be treated adequately due to the immense computational cost. The computations therefore do not account thoroughly for conformational flexibility and solvent dynamics. This manifests in a counterintuitive order of computed entropies ΔS_d^{298} with lower values for ⁱPr and Cy [68 and 74 cal mol⁻¹ K⁻¹] than for Me, ⁱBu, Ad, and Ph [79, 82, 89, and 93 cal mol⁻¹ K⁻¹], respectively.

Solubility proves as a decisive factor that is not taken into account properly by the computations. The most promising candidate $Ad-\mathbf{1}_2$ is almost too poorly soluble to be examined by NMR while all smaller alkyl derivatives R-**1** were readily soluble. The all-*meta* phenyl trityl scaffold (Ph-**1** • etc.) was not sufficiently soluble to be examined in cyclohexane.

Conclusions

We present the synthesis and spectroscopic as well as computational analysis of a series of all-*meta* substituted triphenylmethyl radicals R-**1**[•] with R = Me, ⁱPr, ⁱBu, Cy, and Ph, including the very challenging 1-adamantyl derivative. Beyond the two known, unbridged hexaphenylethane derivatives ^tBu-**1**₂ and hexa(2,6-di-*tert*-butyl-4-biphenylyl)ethane⁴⁶ we were able to observe one new HPE derivative, namely Ad-**1**₂.

En route to the all-meta substituted triphenylmethyl radicals we also synthesized the hydrocarbon- (R-19), alcohol- (R-3), halide- (R-4/R-18), peroxo- (R-20) and carbocation (R-21) derivatives; several of their structural features are also affected by LD interactions. Two rotamers were found for R-19 in the SC-XRD, while only the B-type was identified for all other triphenylmethyl (TPM) species. The B-type rotamers of Me-, ^tBu-, and Cy-**19** form head-to-head dimers that engage in short H---H contacts between the central C--H groups with the shortest being for ^tBu.^{3w} Similarly, for ^tBu- and Cy-**3** we found head-to-head dimers in the SC-XRD, whose formation is supported by red shifted O-H stretching band in the ATR-IR spectra. Peroxides R-20 show no obvious structural evidence for particular strain, not even for Ad-20. In contrast, a better structural fit between bulky (spherical) than between small (or "flat") substituents indicates stronger interactions within the Ad and ^tBu than within the ⁱPr, Cy, and Ph derivatives. This provides hints as to select and utilize dispersion energy donors in the design of structures and catalysts.

NMR spectroscopy of the series of R-**3**, R-**4**, R-**19**, and R-**20** show only a narrow range of chemical shifts with a downfield trend with increasing substituent size – a hint for increasing radical stabilization. Similarly, UV-Vis spectroscopy of R-**21** show a small red shift in λ_{max} indicating a slight increase of the HOMO-LUMO gap and stabilization of the carbocations.

EPR spectroscopy and ρ_{spin} computations for R-1 also show only little changes in the series from Me to Ad but a slight trend for radical stabilization with increasing substituent size. These small spectroscopic changes reveal, in accord with linear free energy relationship parameters for induction/resonance^{38b} and radical stabilization,58 а negligible electronic effect on the trityl scaffold, thereby slightly favoring (R-1)₂ or R-1 over R-1₂. Hence, changes in the stability of $R-\mathbf{1}_2$ must predominantly be governed by changes in London dispersion.

Our conceptually improved computational analysis takes a possible equilibrium between R-1₂, (R-1[•])₂, R-1[•], and R-22 into account and agrees well with experiment: Only parent H-1[•] is in equilibrium with observed H-22⁵⁹ while ^tBu-1[•] and (^tBu-1[•])₂ are almost isoenergetic with the experimentally observable ^tBu-1₂.^{21, 60} For the larger Cy, Ph, and Ad substituents the fully dissociated R-1[•] is energetically highly unfavorable and only R-1₂ and (R-1[•])₂ equilibrate.

The absence of HPE derivatives other than 'Bu-1₂ and Ad-1₂ –obviously the sterically most demanding– emphasizes the importance of the structural match between the interacting "molecular halves" 'Bu-1' or Ad-1' and the necessary small entropic change upon association. Ad-1₂ is experimentally somewhat more stable than 'Bu-1₂ owing to its increased polarizability and high rigidity. Hence, rigidity and symmetry of the substituents contribute to the overall molecular stability and should be considered in structure design with London dispersion interactions, in particular, in catalysis.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. The SI contains computational and experimental procedures and original spectra as well as XYZ coordinates for all computed species, *Mathematica* outputs as well as SC-XRD data as PDF file. Crystallographic data were deposited at the Cambridge Crystallographic Data Centre as CCDC 1851902-1851919 and 1852233.

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Notes

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The authors declare no competing financial interests.

ACKNOWLEDGMENT

We thank Sebastian Ahles (Justus Liebig University Giessen) for very valuable discussions and Andrey A. Fokin (Igor Sikorsky Kyiv Polytechnic Institute and Justus Liebig University Giessen) for instructive questions. We thank Vladyslav Bakhonskyi and Finn Wilming (both Justus Liebig University Giessen) for their preliminary synthetic contributions. We acknowledge Heike Hausmann (Justus Liebig University Giessen) for support with NMR spectroscopy, Astrid Spielmeyer (Justus Liebig University Giessen) with mass spectrometry, Olaf Burghaus (Philipps-University Marburg) with EPR and Christian Logemann (Justus Liebig University Giessen), Victor G. Young Jr., Ph.D. (University of Minnesota) as well as Frank Hampel (Friedrich-Alexander University Erlangen-Nürnberg) with SC-XRD structure elucidation. This work was supported by the Priority Program "Dispersion" (www.spp1807.de) of the Deutsche Forschungsgemeinschaft.

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