

High Dipole Moments

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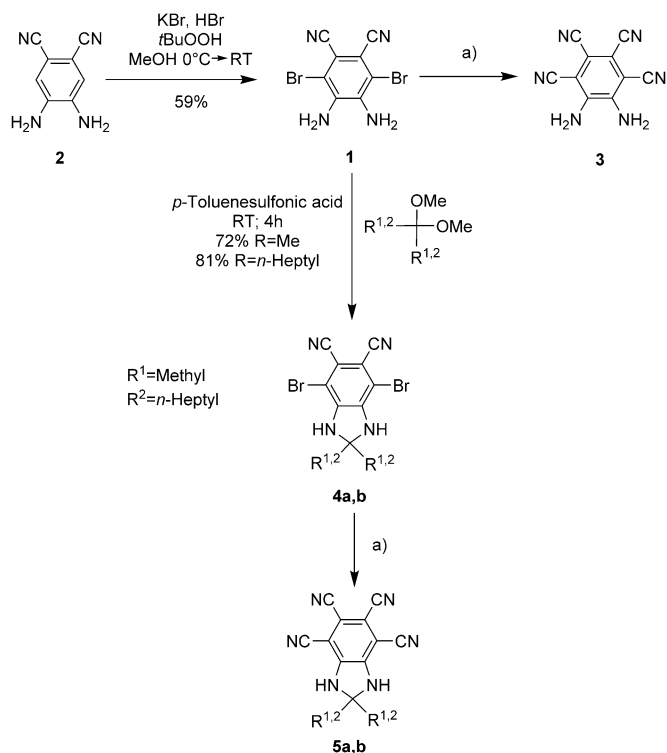
Hexasubstituted Benzenes with Ultrastrong Dipole Moments

Jakob Wudarczyk, George Papamokos, Vasilis Margaritis, Dieter Schollmeyer, Felix Hinkel, Martin Baumgarten, George Floudas, and Klaus Müllen*

Abstract: Hexasubstituted benzenes have been synthesized with the highest known dipole moments, as determined by dielectric spectroscopy and DFT methods. Based on the preparation of 4,5-diamino-3,6-dibromophthalonitrile, combined with a novel method to synthesize dihydrobenzimidazoles, these benzene derivatives have dipole moments in excess of 10 debye. Such dipole moments are desirable in ferroelectrics, nonlinear optics, and in organic photovoltaics. Structure determination was achieved through single-crystal X-ray crystallography, and the optical properties were determined by UV/Vis absorption and fluorescence spectroscopy.

Organic molecules with large dipole moments have garnered attention because of their potential applications in ferroelectrics^[1] and in nonlinear optics (NLO).^[2] In addition, the incorporation of strong dipole moments can lead to improved charge separation at the interface of the donor and the acceptor phases in bulk heterojunction solar cells.^[3,4] To generate dipolar benzenes, one can place electron-withdrawing and electron-donating substituents on opposite sides: the stronger the electron pull on the acceptor side and the electron-pull on the donor side, the higher the expected total dipole moment. Aminobenzonitriles with dipole moments in the range 5.0–5.6 debye have already been the subject of NLO and polarizability studies.^[5] Ultrastrong dipole moments can occur in polymethines having permanent ionic moieties or are able to form zwitterionic species.^[5–7] In contrast to these charged polyenes, our approach based on fully functionalizing benzene with the strongest polarizing substituents results in an ultrastrong dipolar aromatic system, which is charge-free, and so the presented molecules define a new chapter in benzene chemistry.

For the first time, we were able to synthesize 4,5-diamino-3,6-dibromophthalonitrile (**1**) by means of oxidative bromination (Scheme 1) of 4,5-diaminophthalonitrile (**2**); common



Scheme 1. Synthesis of hexasubstituted benzene derivatives with ultrastrong dipole moments. a) $[\text{Pd}_2\text{dba}_3]$, $\text{Zn}(\text{CN})_2$, dppf, PMHS, DMAc, or DMSO, 100 °C, 12 h, 41–62 %. dba = dibenzylideneacetone, dppf = 1,1'-bis(diphenylphosphanyl)ferrocene, PMHS = polymethylhydrosiloxane.

methods based on an electrophilic substitution were unsuccessful, even under harsh conditions. In our approach, we utilized in situ generated hypobromic acid^[8] as a more electrophilic species to attack the aromatic structure in **2**. We applied the method of Bedekar and co-workers^[9] to afford the target compound **1** in a yield of 59% under mild conditions. This functionalization can further facilitate the formation of the tetracyano derivative 5,6-diaminobenzene-1,2,3,4-tetracarbonitrile (**3**). Moreover, we found that, in contrast to literature-known methods with dialkylketones^[10], **1** can undergo a ring-closure reaction with dialkoxyalkanes at room temperature to form dicarbonitrile **4** (yield: 72% in the case of methyl, and 81% in the case of *n*-heptyl substituents). Conversion of the bromo substituents of intermediate **1** into cyano groups was not possible by a Rosenmund-von Braun reaction. However, palladium-assisted cyanation^[11] in dimethylacetamide (DMAc) furnished compound **3** in 60% yield, with the pure product obtained by simple precipitation. The tetracyanated dihydrobenzimidazoles 2,2-dimethyldihydrobenzoimidazole **5a** and its 2,2-diheptyl analogue **5b** were

[*] J. Wudarczyk, Dr. F. Hinkel, Prof. Dr. M. Baumgarten, Prof. Dr. K. Müllen
Max-Planck-Institut für Polymerforschung
Ackermannweg 10, 55128 Mainz (Germany)
E-mail: muellen@mpip-mainz.mpg.de

Dr. G. Papamokos, V. Margaritis, Prof. Dr. G. Floudas
Department of Physics
University of Ioannina
451 10 Ioannina (Greece)

Dr. D. Schollmeyer
Institute für Organische Chemie
Johannes-Gutenberg Universität Mainz
55128 Mainz (Germany)

Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under <http://dx.doi.org/10.1002/anie.201508249>.

prepared by the same procedure in yields of 41 % for **5a** and 62 % for **5b**. When the reaction was carried out in DMAc, the solid tetracyanonitrile **3** always contained residual solvent, as seen by solution NMR spectroscopy and the crystal structure (Figure S3 in the Supporting Information). DMSO was also chosen as the solvent for the cyanation reaction, since it produced weaker complexes with compound **3** (see Figure S5).

The respective optical gaps were determined from the UV/Vis spectra (see Figure 1 and Table 1). The introduction of alkyl chains to dihydrobenzimidazole **4b** facilitated the

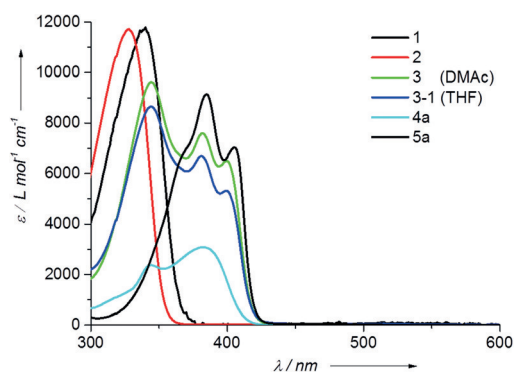


Figure 1. Comparison of the UV/Vis spectra of **1–5a** in THF solutions ($c = 10^{-5} \text{ mol L}^{-1}$).

processing of thin films on a glass substrate and allowed measurement of the absorption in the bulk phase. A bathochromic shift of the absorption by 45 nm in going from solution ($\lambda_{\text{max}} = 387 \text{ nm}$) to the bulk ($\lambda_{\text{max}} = 423 \text{ nm}$, see Figure S35) was found, while **5b** showed only a slight bathochromic shift of 7 nm under the same conditions (Figure S37). Typically, H-type aggregates are known to be formed from cyanine dyes, which give a strong hypsochromic

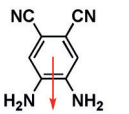
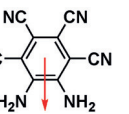
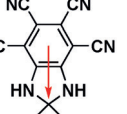
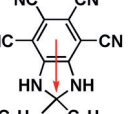
shift and induce fluorescence quenching.^[6] The tetracyanated compounds **3** and **5** exhibited strong blue fluorescence with quantum yields of 48 % (see Table S2), thus emphasizing that there is no strong aggregation.

The geometries of molecules **1–5b** (Table 1) were optimized with tight optimization criteria at the DFT-B3LYP^[12–15] levels of theory with the aug-cc-pVTZ^[16–18] (**1–5a**) basis set. This combination has been shown recently to produce a good correlation between theoretical and experimental results with respect to dipole moments and polarizabilities.^[19] The root mean square deviation (RMSD) and the mean absolute error (MAE) with respect to the experimental results for the calculated dipole moments are 0.12 and 0.09, respectively, while the RMSD and the MAE values are 0.30 and 0.18 for the calculated polarizabilities. Moreover, the adopted level of theory and basis has a comparable performance as MP2/aug-cc-pVTZ and CCSD/aug-cc-pVTZ.

The experimental dipole moments were evaluated from dielectric spectroscopic measurements performed at 25 °C using a Novocontrol Alpha frequency analyzer (frequency range from 10^{-2} to 10^7 Hz). Measurements of the complex dielectric permittivity $\epsilon^* = \epsilon' - i\epsilon''$ (where ϵ' is the real and ϵ'' is the imaginary part) were made with a BDS1308 liquid parallel plate sample cell.^[20] Dilute solutions in THF, and for molecule **5b** also in chloroform, were prepared and the dielectric permittivity was measured as a function of solute concentration (Figure 2). Following the formalism of Böttcher^[21–23] and assuming ideal solutions of the two components, the dipole moment of the solute could be obtained from the derivative of ϵ_{12} with respect to the concentration at the limit of infinite dilution (Table 1 and see the Supporting Information).

The theoretical treatment in vacuo corroborated the steps taken in the synthetic route in terms of the dipole moments as well as the HOMO–LUMO energies. A general finding, stemming both from the DFT calculations performed in vacuo and from the solution experiments, is that the dipole

Table 1: Molecular structures, calculated HOMO–LUMO (eV), experimental optical gap (eV), calculated and measured dipole moments (D), and calculated polarizabilities of the molecules studied herein.^[a]

						
	1 $\text{C}_8\text{N}_4\text{H}_4\text{Br}_2$	2 $\text{C}_8\text{N}_4\text{H}_6$	3 $\text{C}_{10}\text{N}_6\text{H}_4$	4a $\text{C}_{11}\text{N}_4\text{H}_8\text{Br}_2$	5a $\text{C}_{11}\text{N}_6\text{H}_8$	5b $\text{C}_{25}\text{N}_6\text{H}_{30}$
calcd LUMO [eV]	−2.4	−2.0	−3.4	−2.3	−3.0	−2.9
calcd HOMO [eV]	−6.8	−6.6	−7.4	−6.3	−6.8	−6.6
calcd $\Delta E(\text{HOMO-LUMO})$ [eV]	4.4	4.6	4.0	4.0	3.8	3.7
exp. optical gap [eV]	3.4	3.5	3.0	3.0	3.0	2.9
calcd dipole moment [D]	9.6	10.0	9.6	11.5	12.3	12.7
calcd total mol. polarizability [$\times 10^{40} \text{ C}^2 \text{ m}^2 \text{ J}^{-1}$]	29.2	21.9	27.9	35.3	34.2	57.9
exp. dipole moment [D]	12.3 ± 0.4	10.5 ± 0.2	$14.1 \pm 0.7^{[b]}$	12 ± 1	10.9 ± 0.3	12.2 ± 0.3 $11.9 \pm 0.2^{[c]}$

[a] Level of theory: DFT-B3LYP, basis set: aug-cc-pVTZ for molecules **1–5a** and 6-311 + + G(d,p) for molecule **5b**. The arrows represent the direction of the calculated dipole moment (not proportional to its magnitude). The experimental dipole moments were measured in THF. **5b** was also measured in chloroform solution. [b] The higher dipole moment reflects complex formation with DMAc. [c] Measured in chloroform solution.

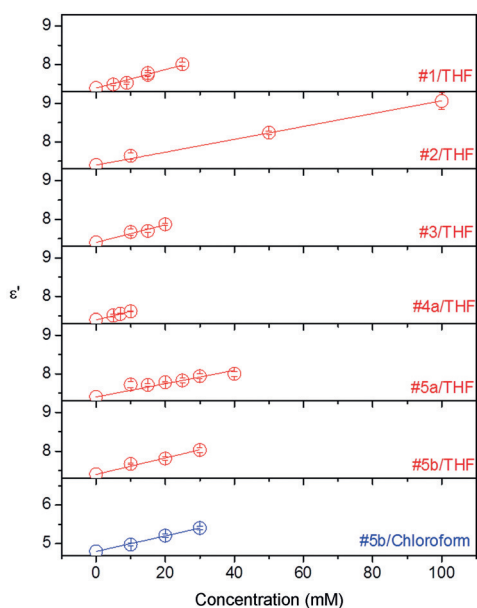


Figure 2. Dielectric permittivity as a function of concentration for **1–5b** in THF (red symbols) and for **5b** in chloroform (blue symbols) solutions. The highest concentrations refer to the solubility limit of each compound. The lines represent linear fits to the $\epsilon'(c)$ data. The respective dipole moments were calculated from the slopes.

moments of all the benzene derivatives are above 9.3 debye (DFT) and 10.5 debye (experiment; Table 1). The highest calculated dipole moment was obtained for **5b**, whereas the highest measured dipole moment was for **3** (the compound having the ability to form a complex with DMAc; see Figure S3). The dihydrobenzimidazoles **4a**, **5a**, and **5b** are expected to show an increase in their dipole moments on alkyl substitution and planarization of the molecule through ring closure, which is supported by the calculated values. Notably, these molecular dipole moments exceed those of disubstituted benzenes (4-nitro-*N,N*-dimethylaniline, $\mu \approx 7$ debye),^[24] of stilbene derivatives ($\mu \leq 7$ debye),^[5] and even of tetrasubstituted benzenes/pyrazines with a variety of donor/acceptors ($\mu \leq 11$ debye).^[25] Since the smallest dipole moment is higher than about 10 debye, hexasubstituted benzene derivatives with a combination of amino and cyano groups can be considered to be the smallest neutral molecular species with the largest dipoles known today.

The highest values of the static isotropic molecular polarizabilities (Table 1) are observed for molecules that carry additional methyl groups and this is indicative of the additivity of this molecular property.^[26] The polarizability of **5b**, upon substitution of methyl groups by alkyl chains, increases significantly with respect to molecule **5a**. Substitution of hydrogen atoms by selected groups at the *o*-positions to the amino groups increases the molecular polarizability, with bromine being the most effective substituent.

The experimental values of the dipole moments generally exceed the ones calculated by DFT, which may result from some remaining solvent contribution to the polarization. To analyze the influence of different solvents, **5b** was synthesized with solubilizing alkyl chains to enable the use of less polar

solvents. The experimental results show a slightly higher dipole moment in the more polar solvent (THF) than in chloroform. Likewise, DFT results performed in vacuo and in solution can vary significantly with respect to the electric properties, such as the polarizability. Consequently, a similar calculation was carried out for **2**: Solvation effects were simulated by the SMD^[27] implicit solvation model at the DFT-B3LYP level of theory and aug-cc-pVTZ basis set. The calculated polarizability of **2** in THF was $31.0 \times 10^{-40} \text{ C}^2 \text{ m}^2 \text{ J}^{-1}$, namely, 42% higher than the value in vacuo, while the computed dipole moment was 14.0 debye.

HOMO–LUMO energies (also given in Table 1 and the Supporting Information) are indicative of the ability of a molecule to donate or accept an electron, and are thus relevant in the present context. The B3LYP functional is widely employed to observe the trends of energy modulation upon alternating the donor–acceptor groups, although the experimental and theoretical determination of HOMO–LUMO energies has stimulated discussions.^[28]

Another important consequence of this study is that it paves the way for strongly electron-deficient compounds to be employed as building blocks in donor–acceptor polymers. Benzothiadiazole has been widely used as an acceptor,^[29–31] whose incorporation into polymers would require bromine atoms in positions 4 and 7. At the same time, one would want to build in electron-withdrawing groups such as nitrile functions at positions 5 and 6. The reaction of diaminobenzene **1** with thionyl chloride readily afforded 4,7-dibromobenzo-*c*[[1,2,5]thiadiazole-5,6-dicarbonitrile (**6**). The potential of the present method can be shown by its subsequent transformation into the dithienyl derivative **7** (Figure 3). The synthesis of **7** was reported recently through a different, less-straightforward route.^[32] Within this oligoaryl derivative, the cyano groups further increase the electron-withdrawing ability of the acceptor without experiencing significant steric strain from the neighboring thienyl substituents. Our current efforts focus on polymerizing the dibromo derivative of **7** with donors, which will be published in the near future.

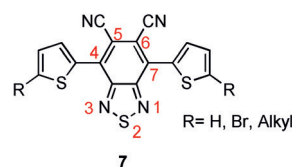


Figure 3. Structure of **7**, including numbering of the positions.

In conclusion, the synthesis of novel benzene derivatives with dipole moments exceeding 10 debye by functionalization of diaminophthalonitrile to its brominated and tetracyanated derivatives is reported. Furthermore, we demonstrated a new synthetic route towards dihydrobenzimidazoles through the use of acetals instead of ketones under mild conditions. Dielectric spectroscopy measurements performed in solution together with DFT calculations performed in vacuo revealed that the designed molecules have ultrastrong dipole moments. Potential applications range from organic electronics such as in ferroelectrics, to nonlinear optics, and to dopants for

organic photovoltaics. To this end, blending organic semiconductors with molecules **1–5** that have ultrastrong dipole moments will lead to an enhanced efficiency of charge separation by decreasing the exciton binding energy.

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Keywords: aromatic substitution · dielectric spectroscopy · dihydrobenzimidazoles · dipole moments · donor–acceptor systems

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