Synthesis and Properties of 2,3-Dihydro-1*H*-corannuleno[2,3-*cd*]pyridine (=2,3-Dihydro-1*H*-dibenzo[1,10:6,7]fluorantheno[3,4-*cd*]pyridine) Derivatives: Heterocyclic *peri*-Anellated Corannulenes

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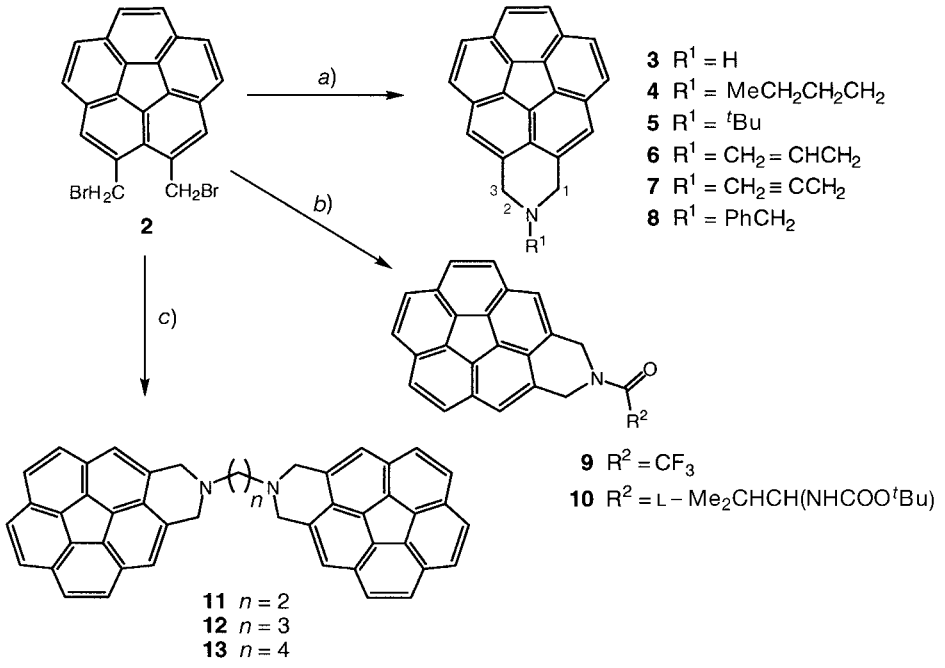
The anellation of a 6-membered ring to the 2,3-position of corannulene (=dibenzo[*ghi*,*mno*]fluoranthene; **1**) leads to curved aromatic compounds with a significantly higher bowl-inversion barrier than corannulene (see *Fig. 1*). If the bridge is $-CH_2-NR-CH_2-$, a variety of linkers can be introduced at the N(2) atom, and the corresponding curved aromatics act as versatile building blocks for larger structures (see *Scheme*). The locked bowl, in combination with an amide bond (see **9** and **10**), gives rise to corannulene derivatives with chiral ground-state conformations, which possess the ability to adapt to their chiral environment by shifting their enantiomer equilibrium slightly in favor of one enantiomeric conformer. Rim annulation of corannulene seems to display a significantly lower electron-withdrawing effect than facial anellation on [5,6]fullerene-C_{60}-I_h, as determined by an investigation of the basicity at the N-atom of $CH_2-NR-CH_2$ (see **4** *vs.* **15** in *Fig. 2*).

1. Introduction. – Control of substitution on corannulene (=dibenzo[*ghi*,*mno*]-fluoranthene; **1**) is fundamental to any strategy using that ring skeleton as a building block toward supramolecular constructs [1][2] or functional fullerene fragments [3–6]. The grafting of new fused rings expands the central ring system, provides sites for ligation, and perturbs the physical properties of corannulene [7–9]. In particular, a three-atom bridge spanning the 2,3 (*peri*) positions of **1** can restrict the dynamic motion of the bowl. If the specific bridge is CH_2NHCH_2, there is a convenient site for substitution at the N-atom. The presence of an amine group in the ring adds functionality to the molecule, and the perturbation of this function (*i.e.* basicity) can serve as a gauge of interactions between the aromatic central polycycle and the functional group. Comparison of the pK_a of an amine in this setting with an amine of similar constitution attached to the rim of a flat aromatic polycycle like naphthalene or the surface of a fullerene like [5,6]fullerene-C_{60}-I_h provides insight to the lone-pair/aromatic-orbital interactions; for example, a related anellation on the surface of fullerene-C_{60}, stemming from an azomethine ylide dipolar cycloaddition, was noted to have reduced basicity at the N-atom, although it was not quantified [10][11]. The redox and orbital properties of corannulene (*e.g.* ionization potential (*IP*) or UV absorption) could also serve as indicators of perturbations. In addition, for appropriately restricted systems, an equilibrium of enantiomeric bowl isomers should display a *Pfeiffer* effect when conjugated to a chiral enantiomerically pure end group [12]. Herein we study the synthesis, dynamics, and physical properties of a series of 2-substituted 2,3-dihydro-1*H*-corannuleno[2,3-*cd*]pyridines (=2,3-dihydro-1*H*-dibenzo[1,10:6,7]fluorantheno[3,4-*cd*]pyridines) by experimental and *ab initio* quantum-mechanical methods.

2. Synthesis of 2-Substituted 2,3-Dihydro-1*H*-corannuleno[2,3-*cd*]pyridines. – The recently developed liquid-phase synthesis of 2,3-dimethylcorannulene [7] provides access to further *peri*-substituted corannulene derivatives. Photobromination of 2,3-dimethylcorannulene by *N*-bromosuccinimide yielded 2,3-bis(bromomethyl)corannulene (**2**) as starting material for the construction of the 6-membered ring anellated compounds **3**–**13** (*Scheme*). For the synthesis of the secondary amine **3**, 2,3-bis(bromomethyl)corannulene (**2**) was treated with an excess of ammonia in 1,2-dimethoxyethane (*ca.* 50% yield). The cyclization to the simple 2-substituted compounds **4**–**8** was accomplished by reaction of **2** with 1 equiv. of the corresponding primary amines R^1NH_2. In this manner, alkyl, aryl [13], allyl, propargyl, and benzyl derivatives were easily accessed. Amides **9** and **10** were obtained by a similar procedure with trifluoroacetamide and (+)-N^2-[(*tert*-butoxy)carbonyl]-L-valinamide, respectively. In these procedures, NaH was used to deprotonate the amides and increase their reactivity in nucleophilic substitution reactions. The 2,2′-(alkane-α,ω-diyl)bis[2,3-dihydro-1*H*-corannuleno[2,3-*cd*]pyridines] **11**–**13** were obtained by reaction of 2 equiv. of **2** with 1 equiv. of the corresponding diamine.

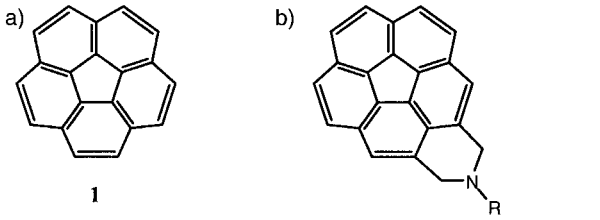
Scheme



a) R^1NH_2 (1 equiv.), THF, pyridine, 60°, 3–5 h. *b*) R^2NH_2 (1 equiv.), NaH (4 equiv.), THF, 60°, 2–3 h. *c*) $H_2N(CH_2)_nNH_2$ (1 equiv.), NaH (4 equiv.), THF, 60°, 3 h.

3. Physical Properties. – *Bowl-Inversion Barrier.* Corannulene (**1**) possesses a barrier of inversion of 11.5 kcal/mol (*Fig. 1,a*), as determined previously in our group by experimental estimates (calc. 11.0 kcal/mol) [14–16] and elsewhere [17–19].

However, 2,3-dimethylcorannulene is predicted by *ab initio* calculations to display a lower bowl inversion barrier of 9.6 kcal/mol (the corresponding experimental value for 2,3-bis(bromomethyl)corannulene is 9.1 kcal/mol). Presumably steric repulsions across the *peri*-position are largely responsible for a flattening of the bowl and hence lead to a lower energetic barrier of bowl inversion [13].



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1; $\Delta G^{inv.}$ = 11.5 kcal/mol **3** R = H; $\Delta G^{inv.}$ = 16.1 kcal/mol
4 R = $MeCH_2CH_2CH_2$;
$\Delta G^{inv.}$ = 16.6 kcal/mol

Fig. 1. a) *Bowl-shaped corannulene* (**1**) *with an inversion barrier of 11.5 kcal/mol*; b) *corannulene derivatives* **3** *and* **4** *with higher bowl-inversion barriers* (>16 kcal/mol)

To investigate the influence of the anellated 6-membered ring on the inversion barrier of the corannulene moiety, we carried out variable-temperature NMR experiments with **3** and **4**. In the static bowl conformer, the geminal CH_2 protons are diastereotopic and give rise to a *dd*. From chemical-shift difference, the geminal coupling constant, and the coalescence temperature of the 6-membered-ring CH_2 protons, one can use the theory of dynamic NMR spectroscopy [20] to deduce an inversion barrier of 16.1 and 16.6 kcal/mol for **3** and **4**, respectively. Similar work on 2-phenyl-2,3-dihydro-1*H*-corannuleno[2,3-*cd*]pyridine revealed a barrier of 16.7 kcal/mol [13]. This activation energy corresponds to a rate constant of the order of 1 s^{-1} as opposed to 10^6 s^{-1} for the untethered **2**. *Ab initio* quantum-mechanical computations on the ground-state structure of **3** and its transition state to bowl inversion predict an enthalpy of activation of 16.4 kcal/mol, in good agreement with experiment. As noted above, such computations on **2** predicted a barrier of 9.6 kcal/mol. Thus, in contrast to simple 2,3-disubstituted corannulene derivatives, the *peri*-anellation of a 6-membered ring on to corannulene significantly increases the bowl-inversion barrier.

Basicity of the N-Atom of **4** *and* **15**. To investigate how the curvature of a polynuclear aromatic hydrocarbon (PAH) affects proximal-rim functional groups, we determined the relative basicity of tertiary amine **4** (R = Bu), 2-butyl-2,3-dihydro-1*H*-benz[*d*,*e*]isoquinoline[1]) (**14**) [21], and 1′,5′-dihydro-2′-methyl-2′*H*-[5,6]fullereno-C_{60}-I_h-[1,9-*c*]pyrrole (**15**) [10][22] (see *Fig. 2*) by means of a competitive titration method, which can be followed by ^{1}H-NMR [23][24]. From the measured changes in the chemical shifts of a mixture of compounds A and B, the ratio of acidity constants K_a^A/K_a^B can be determined by *Eqn. 1*. Plots of $(\delta_B - \delta_B{}^0)(\delta_A{}^+ - \delta_A)$ *vs.* $(\delta_A - \delta_A{}^0)(\delta_B{}^+ - \delta_B)$

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[1]) New data: ^{1}H-NMR (300 MHz, $CDCl_3$): 7.57 (*d*, *J* = 8.1, 2 H); 7.29 (*t*, *J* = 8.1, 2 H); 7.09 (*d*, *J* = 6.9, 2 H); 3.876 (*s*, 4 H); 2.57 (*t*, *J* = 7.8, 2 H); 1.60 (*m*, 2 H); 1.38 (*m*, 2 H); 0.932 (*t*, *J* = 7.1). ^{13}C-NMR (100 MHz, $CDCl_3$): 133.37; 132.96; 128.09; 125.89; 125.44; 121.85; 57.62; 56.97; 29.65; 20.91; 14.26.

are linear with zero intercept and a slope of K_a^A/K_a^B; δ_A^0, δ_B^0, δ_A^+, and δ_B^+ are the limiting chemical shifts of unprotonated and protonated forms of compounds A and B.

$$(\delta_B - \delta_B^{0)}(\delta_A^+ - \delta_A) = (K_a^A/K_a^B)(\delta_A - \delta_A^0)(\delta_B^+ - \delta_B) \quad (1)$$

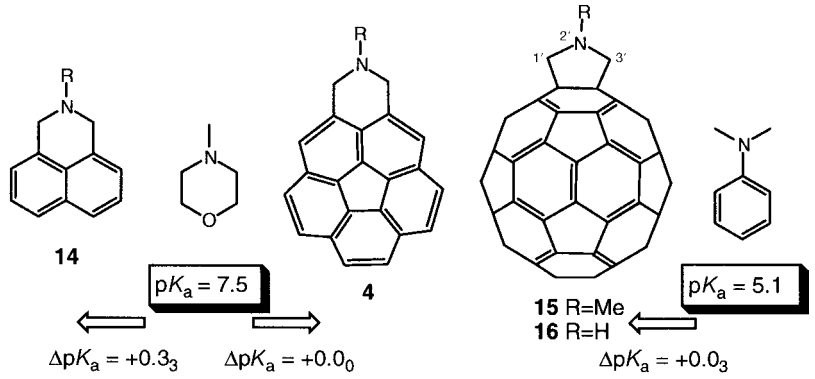

Fig. 2. *Relative basicity of amines* **4**, **14**, *and fullereno-C_{60}-pyrrole* **15**

The influence of the aromatic segment on the pK_a values of the tertiary amines **4**, **14**, and **15** could be judged by comparing the pK_a values obtained with those of reference compounds like *N*-methylmorpholine and *N*,*N*-dimethylaniline. From the linear correlation ($R > 0.99$) depicted in *Fig. 3*, it was deduced that the corannulene derivative **4**, in $CDCl_3$, is only slightly less basic than amine **14**, and both display a basicity similar to *N*-methylmorpholine (pK_a(aq) 7.41) [25]. Constitutionally, **4** and **14** are akin to dibenzylmethylamine (pK_a 8.8) where the benzene rings of the benzyl groups have become fused, but the present results would place them at lower basicity than tribenzylamine (pK_a 8.3) and 3–4 pK units lower than triethylamine (pK 10.7). On the other hand, dihydro-*N*-methylfullereno-C_{60}-pyrrole **15** exhibits an even lower basicity, and, in $CS_2/CHCl_3$, is comparable to *N*,*N*-dimethylaniline (pK_a(aq) 5.1) [26]. Although the absolute pK_a values for these compounds are solvent-dependent, the pairwise competitions provide a good relative sense of the basicity in a common environment. From these data it can be concluded that facial anellation of fullerene-C_{60} results in a far stronger electron-withdrawing effect through n-π interactions than rim anellation on the fullerene fragment corannulene. As a side note, if **4** and **15** were soluble in H_2O, **4** would be roughly 50% protonated, whereas **15** would be essentially completely unprotonated at physiological pH.

To probe these acid/base effects further, an *ab initio* quantum-mechanical computational study of the protonation of the *N*-unsubstituted **3** and **16** was carried out (*cf. Sect. 5*). The structure and energy for the neutral and protonated form were calculated, zero-point-energy corrections were made on the basis of the computed normal modes, and quantum-mechanical solvation energies were included to allow comparison with the solution-phase work (*Table*). The gas-phase computational data qualitatively agree with that obtained from experiment. The relative energies of proton affinity for *N*-methylmorpholine and **3** cluster together as compared to the values for aniline, *N*,*N*-dimethylaniline, and **16**. The ranking of the two clusters correctly assigns

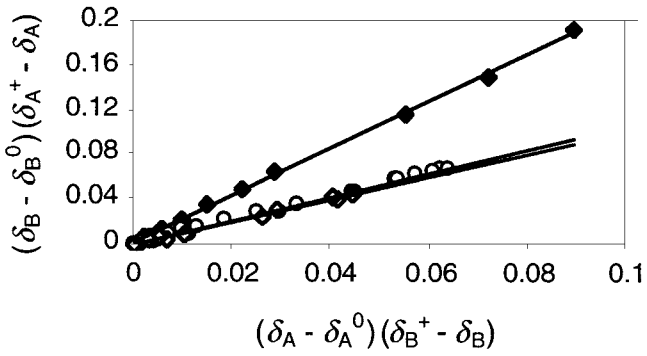

Fig. 3. *Linearized plots of* $(\delta_B - \delta_B^0)(\delta_A^+ - \delta_A)$ vs. $(\delta_A - \delta_A^0)(\delta_B^+ - \delta_B)$ for **15** *and* N,N-*dimethylaniline* (○), for **4** (◇), *and for* N-*methylmorpholine* **14** (◆)

the former as more basic. In addition to the similarity in energy, there are also structural features at the N-atom that correlate for the two clusters. Whereas *N*-methylmorpholine and **3** display distinct pyramidal geometry at the N-atom, **16** and *N*,*N*-dimethylaniline exhibit a planar N-atom indicating that the n-π interactions between the fullerene-C_{60} and N orbitals are strong enough to warrant rehybridization at the N-atom to sp^2. This mixing is also apparent in the molecular orbitals of **16**, where the first MO displaying significant contribution from the N-atom is burried at HOMO-6 (– 9.3 eV); the comparable orbital for **3** is HOMO-1 (– 7.8 eV) (see *Fig. 4*). First ionization potentials (*IP*) assessed by ΔSCF computation are not particularly good predictors of solution p*K* values in this series, because the HOMO does not always have a contribution from the N-atom. Differential solvation of the ions plays a significant role in the overall reaction energetics in solution; the computational results are preliminary, and a more detailed analysis will be presented later.

Table 1. *Computational Data for* **3** *and* **16**. *IP* = ionization potential; *P.A.* = proton affinity; *ZPE* = zero-point energy.

Property	Aniline	*N*,*N*-Dimethylaniline	*N*-Methylmorpholine	**3**	**16**
IP (ΔSCF) [eV]	– 7.7	– 6.9	– 8.1	– 7.3	– 7.1
P.A. (g)[a]) [kcal/mol]	221.5	234.9	239.5	241.9	233.9
P.A. + *ZPE* (g)[a]) [kcal/mol]	212.4	225.6	228.8	232.3	224.0
ΔG(A)[b]) [kcal/mol]	– 8.38	– 6.65	– 7.74	– 15.00	– 3.8
ΔG(AH^+)[b]) [kcal/mol]	– 66.00	– 56.30	– 64.64	– 66.30	– 61.7
p*K*[c])	2.5	6.2	13.9	12.4	11.16

[a]) *P.A.* (g) = *E*(neutral) – *E*(cation). [b]) *E*(solvation). [c]) [*P.A.* + $\Delta\Delta G$(solvation) + ΔG(H^+ solvation)]/1.36.

Chiral Corannulene Derivatives. The static conformations of amides **9** and **10** have C_1 symmetry. The 2,3-dihydro-2-(trifluoroacetyl)-1*H*-corannuleno[2,3-*cd*]pyridine (**9**) consists of two enantiomeric conformations, which can be interconverted either *via* bowl inversion ($\Delta G \approx 16$ kcal/mol) or amide rotation ($\Delta G \approx 18$ kcal/mol). The bowl-inversion process, which is slow at room temperature, in combination with hindered amide-bond rotation gives rise to molecules with an inherent ability to adapt to their

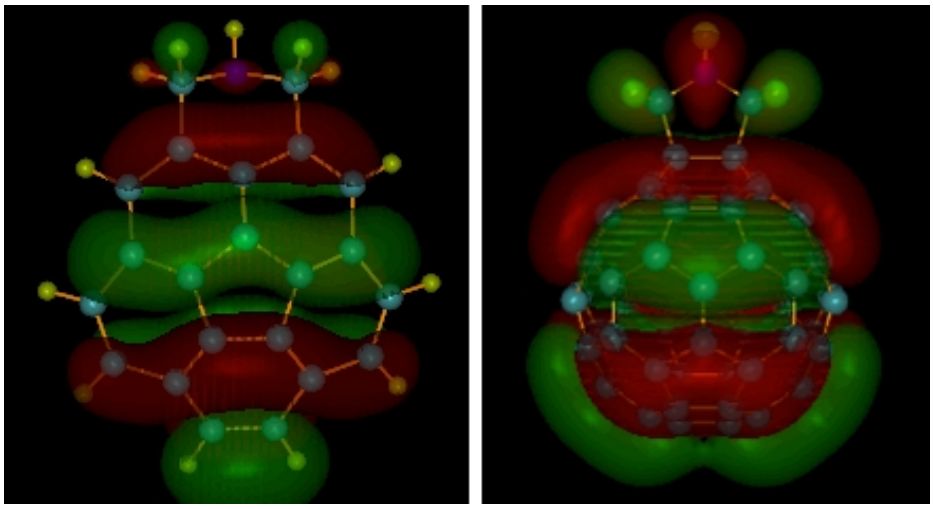

Fig. 4. *Image of HOMO-6 for* **16** *and HOMO-1 for* **3**

chiral environment by shifting the equilibrium towards one of the enantiomeric forms. Amide **10**, which was obtained by reaction of the 2,3-bis(bromomethyl)corannulene with (+)-*N*-Boc-L-valinamide [27], consists of a mixture of two diastereoisomers that must differ in energy, albeit slightly, and this should manifest a signal in the CD due to the corannulene chromophore. The CD of (+)-*N*-Boc-L-valinamide gives a very weak spectrum in the form of a *Drude* curve over the range 220–360 nm. However, this same chiral and enantiomerically pure moiety of L-valine in molecule **10** has a clear influence on the corannulene bowl/amide-bond conformation, as was indicted by the appearance of a *Cotton* effect in the CD spectrum of **10**[2]).

*2,2′-(Ethane-1,2-diyl)-, 2,2′-(Propane-1,3-diyl)-, and 2,2′-(Butane-1,4-diyl)bis[2,3-dihydro-1*H*-corannuleno[2,3-cd]pyridine]* (**11**, **12**, and **13**, resp.). On the basis of the similar curvature of the concave side of corannulene derivatives like **3** with the aromatic surface of fullerenes and the conceivable increase in π-π interactions between surfaces of matched curvatures, linked corannulene derivatives were prepared to look for fullerene binders. At present, UV-titration experiments and NMR studies of compounds **11**–**13** with fullerene-C_{60} in CS_2 have not indicated any detectable binding. The lack of rigidity of the linker and hence the unfavorable entropy term of association could lead to low association constants, which could not be determined by means of UV experiments due to spectral overlap of **11**–**13** and fullerene-C_{60}, or more importantly, because the poor solubility of **11**–**13** and fullerene-C_{60} makes it difficult to set conditions where any appreciable binding could be seen if K_{eq} was less than 10^3 M^{-1}.

Fluorescence, UV, and IP *Properties.* All derivatives **3**–**13** display UV-absorption spectra comparable to the sum of the parent components. For example, the spectrum of the *N*-benzyl derivative **8** looks like that of 2,3-dimethylcorannulene plus benzylamine.

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[2]) While the CD spectrum at room temperature (220–360 nm) of (+)-*N*-Boc-L-valinamide in $CHCl_3$ does not indicate any CD effects, ellipticity maxima of *ca.* +1.5 mdeg at 310 and 280 nm, and a minimum of −1.5 mdeg at 240 nm can be observed in the CD spectrum of **10**.

Indeed, the UV and fluorescence spectra of **4** and 2,3-dimethylcorannulene are essentially identical [7], indicating that no strong n-π mixing is present in either the ground or the excited state. Computational work on the orbitals of **4** indicates that the HOMO is centered on the lone pair of the N-atom and that the *IP* by ΔSCF methods is predicted to be 7.3 eV, not far from a standard alkylamine.

4. Conclusions. – Access to **2** made the synthesis of 2,3-dihydro-1*H* corannuleno[2,3-*cd*]pyridines relatively straightforward. The addition of a bridge between the *peri*-position raised the barrier to bowl inversion. The N-atom was used as an attachment point for the creation of a number of *N*-substituted derivatives. Trivial chiral analogs were prepared by coupling amino-acid derivatives to the N-atom in the form of an amide linkage; weak chiroptical properties were observed. The *p*K and spectral and molecular-recognition properties were studied. The p*K* measurements on **4** done in comparison to **15** revealed that, although **4** is a weak base compared to triethylamine, **15** is as weak as dimethylaniline due to a strong interaction between the fullerene-C_{60} and n orbitals.

5. Computational Methods. – The conformational analyses of the molecular systems described in this study, including structural and orbital arrangements as well as property calculations, were carried out by means of a variety of computational techniques for comparative purposes, with GAMESS [28] and GAUSSIAN98 [29]. Reported here are the HDFT method, which employed *Becke*'s 3-parameter functional [30] in combination with nonlocal correlation provided by the *Lee-Yang-Parr* expression [31][32] that contains both local and nonlocal terms (B3LYP), and the MP2 method [33]. The DZV (2d,p) double-ζ valence basis set was employed [34]. This basis set includes 2 sets of six d polarization functions on all heavy atoms, and 1 set of p polarization functions on H-atoms. Additional single-point energies were computed using the MP2 correlated methodology, to obtain energies for bowl inversion comparable with experiment. These levels of theory have been previously shown by us and others to be reliable for structural determination in these types of compounds [13].

Geometry optimizations with all methods used tight convergence criterion for SCF calculation and r.m.s gradient (10^{-6} a.u.). The HDFT calculations used a fine integration grid, the optimal choice for calculational accuracy. From the fully optimized structures, chemical and physical properties including orbital interactions, proton affinities, ionization potentials, and pK_a values, were derived. Barriers to inversion were determined by identifying the transition-state structure (1 imaginary frequency in the Hessian) and subtracting its energy from the ground state evaluated at MP2/DZV(2d,p)//B3LYP/DZV(2d,p). Ionization potentials are calculated using the *Koopmans*-theorem approximation [35] as well as the more accurate ΔSCF computation [36][37]. Proton affinities were calculated as $[E+ZPE]_A - [E+ZPE]_{AH}$ where *ZPE* is the zero-point energy. Molecular-orbital contour plots, used as an aid in the discussion of the results, were generated using the program 3D-PLTORB [38] and depicted using QMView [39]. Solvent computations necessary for computing pK_a values were performed using the polarizable conductor calculation model [40][41] at a dielectric permittivity ε of 78.4, as the value for H_2O at room temperature. These

computations were performed also with fine-grid integration. The nature of each stationary point was uniquely characterized by analytically calculating and diagonalizing the matrix of energy second derivatives (Hessian) to determine the number of imaginary frequencies. From the Hessian for each minimum, the *ZPE*s needed above were calculated.

Experimental Part

General. THF and DME were distilled from CaH_2 and then from Na/benzophenone. CH_2Cl_2 was distilled from CaH_2. All other reagents were used as received from *Aldrich* or *Acros*. TLC: *Whatman AL SIL G/UV$_{254}$*. Flash column chromatography (FC): silica gel (230–425 mesh) from *Fisher Scientific Company*. M.p.: *Mel-Temp* apparatus from *Laboratory Devices*; uncorrected. UV/VIS Spectra: *Perkin-Elmer-Lambda-19* spectrometer; 1-cm cuvettes; λ_{max} (ε) in nm. CD Spectra: *Cary-61* instrument. IR Spectra: *Perkin-Elmer-1420-IR* spectrophotometer; $\tilde{\nu}$ in cm^{-1}). NMR Spectra: *Varian Mercury 300 MHz*, *-400*-MHz, or *-Unity-500* instruments; δ in ppm, J in Hz, internal Me_4Si. Mass spectra were recorded at the UC Riverside mass spectrometry facility in FAB or DEI mode; *m*/*z* (rel. int.).

^{1}H-NMR Titrations. The ^{1}H-NMR spectra of mixtures (6 µmol each) of *2-butyl-2,3-dihydro-1*H-*benz[*d,e*]isoquinoline* (**14**) and *N*-methylmorpholine (resp. of *2-butyl-2,3-dihydro-1*H-*corannuleno[2,3-*cd*]pyridine* (**4**) and *N*-methylmorpholine) in $CDCl_3$ (0.6 ml) or *1′,5′-dihydro-2′-methyl-2′*H-*[5,6]fullereno-C$_{60}$-I$_h$-[1,9-*c*]pyrrole* (**15**) and *N,N*-dimethylaniline in $CS_2/CDCl_3$ 2:1 (0.6 ml) were recorded on a *Varian-500-Unity* spectrometer. To these solns., 10-µl aliquots of 0.2N CF_3COOH in the corresponding solvent were added. After each addition, the chemical shifts of the Me groups of **15** and *N,N*-dimethylaniline, of CH_2(1) of **4** (resp. of CH_2(1) of **14**) and the Me group of *N*-methylmorpholine were measured. After no further change in chemical shifts could be observed, the solns. were titrated back with 0.5M DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) (5-µl aliquots).

*2,3-Dihydro-1*H-*corannuleno[2,3-*cd*]pyridine (=2,3-Dihydro-1*H-*dibenzo[1,10:6,7]fluoranthen o[3,4-*cd*]pyridine*; **3**). NH_3 Gas was bubbled through 1,2-dimethoxyethane (20 ml) at $-30°$ for 15 min before 2,3-bis(bromomethyl)corannulene (**2**; 55 mg, 0.12 mmol) was added at once. The soln. was sealed and allowed to warm to r.t. (1 h) and then heated to 60° for 5 h. After cooling to r.t., the white precipitate was dissolved by adding H_2O (50 ml), and the mixture was extracted with CH_2Cl_2 (2 × 50 ml) and evaporated. FC (silica gel (5 g); CH_2Cl_2/MeOH 10:1) of the residue yielded 17 mg (46%) of **3**. Yellow foam. M.p. 73–76° (dec.). R_f (CH_2Cl_2/MeOH 18:1) 0.11. UV ($c = 2.6 \cdot 10^{-6}$ M, $CHCl_3$): 258 (62400), 293 (29800). IR (KBr): 3400*m*, 2950*w*, 1640*w*, 1450*w*, 1310*w*, 1250*w*, 1100*w*, 820*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.75 (*d*, J = 8.8, 2 H); 7.73 (*s*, 2 H); 7.70 (*d*, J = 8.8, 2 H); 7.39 (*s*, 2 H); 4.71 (*d*, J = 16, 2 H); 4.02 (*d*, J = 16, 2 H); 2.33 (br. *s*, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 138.18; 136.42; 136.20; 135.62; 132.01; 130.37; 128.49; 127.24; 127.04; 126.56; 120.45; 49.25. DEI-MS: 291 (30, M^+), 290 (40, $[M-H]^+$), 259 (15), 230 (17), 218 (19), 204 (100), 191 (92), 145 (13), 55 (21). HR-MS: 290.096313 ($C_{22}H_{12}N^+$; calc. 290.096974).

*2-Butyl-2,3-dihydro-1*H-*corannuleno[2,3-*cd*]pyridine (=2-Butyl-2,3-dihydro-1*H-*dibenzo[1,10:6,7]fluoranthen o[3,4-*cd*]pyridine*; **4**). To a soln. of **2** (44 mg, 0.1 mmol) in dry THF (4 ml), a soln. of butylamine (11 µl, 0.11 mmol) and pyridine (16 µl, 0.2 mmol) in THF (2 ml) was added at r.t. The mixture was heated to reflux for 4 h and then evaporated and the residue purified by FC (silica gel (5 g); CH_2Cl_2/MeOH 50:1): **4** (19 mg, 55%). Pale yellow solid. M.p. 110° (dec.). R_f (CH_2Cl_2/MeOH 10:1): 0.69. UV ($c = 2.52 \cdot 10^{-5}$ M, $CHCl_3$): 257 (63800), 293 (28400). IR (KBr): 3000*w*, 2900*m*, 2850*w*, 1640*m*, 1450*w*, 1360*w*, 1300*w*, 1100*w*, 860*w*, 820*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.74 (*d*, J = 8.8, 2 H); 7.72 (*s*, 2 H); 7.71 (*d*, J = 8.8, 2 H); 7.43 (*s*, 2 H); 4.41 (*d*, J = 14.8, 2 H); 3.79 (*d*, J = 14.8, 2 H); 2.56 (*t*, J = 7.6, 2 H); 1.57 (*m*, 2 H); 1.31 (*m*, 2 H); 0.90 (*t*, J = 7.6, 3 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 136.55; 136.18; 135.89; 132.45; 131.58; 130.41; 127.10; 126.50; 121.81; 56.70; 56.27; 29.56; 20.69; 14.15. DEI-MS: 347 (40, M^+), 346 (28, $[M-H]^+$), 304 (100), 289 (23), 277 (15), 263 (10), 152 (14), 138 (10). HR-MS: 346.158551 ($C_{26}H_{20}N^+$; calc. 346.159575).

*2-(*tert*-Butyl)-2,3-dihydro-1*H-*corannuleno[2,3-*cd*]pyridine* (=*2-(*tert*-Butyl)-2,3-dihydro-1*H-*dibenzo[1,10:6.7]fluoranthen o[3,4-*cd*]pyridine*; **5**). As described for **4**, with **2** (44 mg, 0.1 mmol), THF (5 ml), *tert*-butylamine (15 µl, 0.15 mmol), pyridine (16 µl, 0.2 mmol), and THF (1 ml). FC (silica gel (5 g); CH_2Cl_2/MeOH 99:1) yielded **5** (10 mg, 30%). Yellow oil. R_f (CH_2Cl_2/MeOH 15:1) 0.63. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.72 (*s*, 2 H); 7.71 (*s*, 2 H); 7.70 (*s*, 2 H); 7.44 (*s*, 2 H); 4.39 (*d*, J = 14.1, 2 H); 3.99 (*d*, J = 14.1, 2 H); 1.26 (*s*, 9 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 136.73; 136.66; 136.14; 133.02; 130.76; 127.17; 126.99; 126.33; 121.66; 50.31; 26.59. DEI-MS: 348 (100, MH^+), 332 (15), 292 (18), 178 (10). HR-MS: 348.175712 ($C_{26}H_{22}N^+$; calc. 348.175225).

*2,3-Dihydro-2-(prop-2-enyl)-1*H*-corannuleno[2,3-*cd*]pyridine (=2,3-Dihydro-2-(prop-2-enyl)-1*H*-dibenzo[1,10:6,7]fluorantheno[3,4-*cd*]pyridine*; **6**). As described for **4**, with **2** (44 mg, 0.1 mmol), THF (3 ml), prop-2-en-1-amine (10 µl, 0.15 mmol), EtN^iPr_2 (50 µl, 0.3 mmol), and THF (1 ml). FC (silica gel (5 g), CH_2Cl_2/MeOH 99:1) yielded **6** (15 mg, 45%). Pale yellow solid. M.p. 92–95° (dec.). R_f (CH_2Cl_2/MeOH 10:1) 0.56. UV ($c = 3.45 \cdot 10^{-5}$ M $CHCl_3$): 258 (64800), 293 (29400). IR (KBr): 3000*w*, 2900*m*, 2750*w*, 1640*s*, 1420*m*, 1300*m*, 1095*m*, 990*m*, 850*s*, 820*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.75 (*d*, *J* = 8.8, 2 H); 7.73 (*s*, 2 H); 7.71 (*d*, *J* = 8.8, 2 H); 7.43 (*s*, 2 H); 5.91 (*m*, 1 H); 5.19 (*m*, 2 H); 4.42 (*d*, *J* = 14.8, 2 H); 3.80 (*d*, *J* = 14.4, 2 H); 3.21 (*d*, *J* = 6.4, 2 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 136.52; 136.19; 135.88; 135.07; 132.46; 130.39; 127.09; 127.12; 127.07; 126.48; 121.71; 118.17; 60.32; 56.09. DEI-MS: 331 (100, M^+), 289 (46), 263 (70). HR-MS: 331.135887 ($C_{25}H_{17}N^+$; calc. 331.136100).

*2,3-Dihydro-2-(prop-2-ynyl)-1*H*-corannuleno[2,3-*cd*]pyridine (=2,3-Dihydro-2-(prop-2-ynyl)-1*H*-dibenzo[1,10:6,7]fluorantheno[3,4-*cd*]pyridine*; **7**). As described for **4**, with **2** (44 mg, 0.1 mmol), THF (3 ml), prop-2-yn-1-amine (10 µl, 0.15 mmol), pyridine (16 µl, 0.2 mmol), and THF (1 ml). FC (silica gel (5 g); CH_2Cl_2/MeOH 99:1) yielded **7** (21 mg, 63%). Dark yellow oil. R_f (CH_2Cl_2/MeOH 40:1) 0.65. UV ($c = 3.1 \cdot 10^{-5}$ M, $CHCl_3$): 258 (68200), 294 (30600). IR (KBr): 3260*m*, 3010*w*, 2900*w*, 2760*w*, 1620*w*, 1480*m*, 1300*m*, 1100*m*, 820*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.74 (*d*, *J* = 8.8, 2 H); 7.72 (*s*, 2 H); 7.70 (*d*, *J* = 8.8, 2 H); 7.44 (*s*, 2 H); 4.53 (*d*, *J* = 14.7, 2 H); 3.87 (*d*, *J* = 14.7, 2 H); 3.55 (*d*, *J* = 2.4, 2 H); 2.34 (*t*, *J* = 2.4, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 136.48; 136.12; 135.94; 135.80; 132.47; 130.41; 128.37; 127.12; 127.06; 126.52; 121.63; 78.58; 74.10; 55.01; 46.31. DEI-MS: 329 (100, M^+), 288 (56), 263 (37). HR-MS: 329.120243 ($C_{25}H_{15}N^+$; calc. 329.120450).

*2-Benzyl-2,3-dihydro-1*H*-corannuleno[2,3-*cd*]pyridine (=2-Benzyl-2,3-dihydro-1*H*-dibenzo[1,10:6.7]fluoranthenо[3,4-*cd*]pyridine*; **8**). As described for **4**, with **2** (44 mg, 0.1 mmol), THF (4 ml), benzylamine (12 µl, 0.11 mmol), pyridine (16 µl, 0.2 mmol), and THF (1 ml) (5 h). FC (silica gel (5 g); CH_2Cl_2/MeOH 95:5) yielded **8** (11 mg, 28%). Yellow oil. R_f (CH_2Cl_2/MeOH 40:1) 0.70. UV ($c = 3.1 \cdot 10^{-5}$ M, $CHCl_3$): 258 (61100), 295 (29700). IR (KBr): 3040*w*, 2950*w*, 1640*s*, 1450*m*, 1250*w*, 820*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.75 (*d*, *J* = 8.8, 2 H); 7.73 (*s*, 2 H); 7.70 (*d*, *J* = 8.8, 2 H); 7.39 (*s*, 2 H); 7.29 (*s*, 4 H); 7.25 (*s*, 1 H); 4.44 (*d*, *J* = 14.8, 2 H); 3.82 (*d*, *J* = 14.7, 2 H); 3.70 (*s*, 2 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 136.60; 136.10; 135.88; 132.41; 130.46; 129.09; 128.25; 127.23; 127.12; 126.52; 121.85; 61.50; 56.09. DEI-MS: 381 (25, M^+), 291 (100), 263 (70), 146 (15), 131 (15), 91 (95), 65 (15). HR-MS: 381.150119 ($C_{29}H_{19}N^+$; calc. 381.151750).

*2,3-Dihydro-2-(trifluoroacetyl)-1*H*-corannuleno[2,3-*cd*]pyridine (=2,3-Dihydro-2-(trifluoroacetyl)-1*H*-dibenzo[1,10:6,7]fluorantheno[3,4-*cd*]pyridine*; **9**). To a soln. of **2** (44 mg, 0.1 mmol) in dry THF (4 ml), a soln. of CF_3CONH_2 (12.5 mg, 0.11 mmol) and pyridine (16 µl, 0.2 mmol) in THF (1 ml) and NaH (16 mg, 0.4 mmol) were added at r.t. After heating to reflux for 3 h, the mixture was diluted with CH_2Cl_2 (25 ml) and washed with H_2O (20 ml), the org. phase evaporated, and the residue purified by FC (silica gel (5 g); CH_2Cl_2/MeOH 95:5): **9** (4 mg, 10%). Yellow oil. R_f (CH_2Cl_2/MeOH 50:1) 0.75. UV ($c = 3.1 \cdot 10^{-5}$ M, $CHCl_3$): 258 (60800), 292 (27600). IR (KBr): 2910*m*, 2840*w*, 1695*s*, 1440*m*, 1300*w*, 1200*s*, 1160*s*, 1010*w*, 860*w*, 820*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.81 (*d*, *J* = 8.8, 2 H); 7.78 (*s*, 2 H); 7.76 (*d*, *J* = 8.8, 2 H); 7.60 (*s*, 1 H); 7.53 (*s*, 1 H); 5.40 (*d*, *J* = 16.4, 1 H); 5.33 (*d*, *J* = 15.2, 1 H); 5.23 (*d*, *J* = 15.2, 1 H); 4.94 (*d*, *J* = 16.4, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 136.72; 136.08; 136.04; 135.91; 132.45; 132.33; 132.17; 131.97; 130.86; 130.85; 127.78; 127.75; 127.72; 127.13; 127.10; 126.99; 122.69; 121.84; 49.48; 49.44; 47.26. DEI-MS: 387 (45, M^+), 288 (30), 274 (100), 263 (35). HR-MS: 387.086262 ($C_{24}H_{12}NOF_3^+$; calc. 387.087099).

tert-*Butyl {[(1S)-1-(2,3-Dihydro-1*H*-corannuleno[2,3-*cd*]pyridin-2-yl)-2-methyl]propyl}carbamate* (=tert-*Butyl {[(1S)-(2,3-Dihydro-1*H*-dibenzo[1,10:6,7]fluorantheno[3,4-*cd*]pyridin-2-yl)-2-methyl]propyl}carbamate*; **10**). As described for **9**, with **2** (44 mg, 0.1 mmol), THF (4 ml), (+)-*N*-Boc-L-valinamide (21 mg, 0.1 mmol), pyridine (16 µl, 0.2 mmol), THF (1 ml), and NaH (16 mg, 0.4 mmol) (2 h). Workup with CH_2Cl_2 (20 ml), sat. $NaHCO_3$ soln. (20 ml), and $MgSO_4$ (drying). FC (silica gel (5 g); CH_2Cl_2/MeOH 95:5) yielded **10** (13 mg, 31%). Dark yellow oil. R_f (CH_2Cl_2/MeOH 9:1) 0.8. UV ($c = 1.9 \cdot 10^{-5}$ M, $CHCl_3$): 258 (64000), 292 (31900). IR (KBr): 2950*m*, 1740*s*, 1650*s*, 1490*m*, 1420*w*, 1360*m*, 1240*m*, 1160*s*, 1110*w*, 870*w*, 820*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.90–7.70 (*m*, 6 H); 7.55 (*s*, 2 H); 5.60–4.60 (*m*, 5 H); 2.08–2.01 (*m*, 1 H); 1.45, 1.34 (2*s*, 9 H); 1.10–0.85 (*m*, 6 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 171.45; 156.01; 136.68; 136.67; 136.15; 135.95; 132.78; 130.97; 130.90; 129.03; 127.67; 127.37; 127.22; 127.18; 122.07; 121.81; 121.31; 55.22; 55.18; 49.07; 45.41; 37.76; 31.37; 19.79; 19.71; 19.38; 17.11; 16.90. DEI-MS: 490 (5, M^+), 290 (100), 263 (30), 207 (32), 105 (21), 55 (74). HR-MS: 490.225233 ($C_{32}H_{30}N_2O_3^+$; calc. 490.225643).

*2,2′-(Ethane-1,2-diyl)-, 2,2′-(Propane-1,3-diyl)-, and 2,2′-(Butane-1,4-diyl)bis[2,3-dihydro-1*H*-corannuleno-[2,3-*cd*]pyridine](=2,2′-(Ethane-1,2-diyl)-, 2,2′-(Propane-1,3-diyl)-, and 2,2′-(Butane-1,4-diyl)bis[2,3-dihydro-1*H*-dibenzo[1,10:6.7]fluorantheno[3,4-*cd*]pyridine]*; **11**–**13**, resp.). To a soln. of **2** (44 mg, 0.1 mmol) in dry THF (5 ml), ethane-1,2-diamine (3.4 µl, 0.05 mmol), propane-1,3-diamine (4.5 µl, 0.05 mmol), or butane-1,4-

diamine (5 µl, 0.05 mmol), resp., and NaH (16 mg, 0.4 mmol) were added at r.t. The mixture was heated to reflux for 15 h, diluted with CH_2Cl_2 (20 ml), and washed with H_2O (20 ml). The org. phase was dried ($MgSO_4$) and evaporated. FC (silica gel (5 g), CH_2Cl_2/MeOH 98 :2) of the residue yielded 8 mg (13%) of **11**, 10 mg (16%) of **12**, or 16 mg (25%) of **13**, resp., all as yellow solids.

Data of **11**: M.p. 250° (dec.). R_f (CH_2Cl_2/MeOH 95 :5) 0.45. UV ($c = 9.82 \cdot 10^{-6}$ M, $CHCl_3$): 258 (79300), 293 (38200). ^{1}H-NMR (400 MHz, $CDCl_3$): 7.74 (*d*, *J* = 8.8, 4 H); 7.73 (*s*, 4 H); 7.68 (*d*, *J* = 8.8, 4 H); 7.37 (*s*, 4 H); 4.47 (*d*, *J* = 14.8, 4 H); 3.80 (*d*, *J* = 14.8, 4 H); 2.71 (*s*, 4 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 136.54; 136.10; 136.09; 135.84; 132.32; 130.39; 129.00; 127.10; 127.07; 126.50; 121.78; 56.70; 54.70. DEI-MS: 609 (10, MH^+), 320 (15), 306 (10), 292 (100), 263 (10). HR-MS: 609.236398 ($C_{46}H_{29}N_2^+$; calc. 609.233074).

Data of **12**: M.p. 194 – 196°. R_f (CH_2Cl_2/MeOH 10 :1) 0.15. UV ($c = 2.6 \cdot 10^{-6}$ M, $CHCl_3$): 257 (98300), 292 (42000). ^{1}H-NMR (400 MHz, $CDCl_3$): 7.73 (*d*, *J* = 8.8, 4 H); 7.72 (*s*, 4 H); 7.67 (*d*, *J* = 8.8, 4 H); 7.38 (*s*, 4 H); 4.38 (*d*, *J* = 14.4, 4 H); 3.76 (*d*, *J* = 14.4, 4 H); 2.58 (*t*, *J* = 6.8, 4 H); 1.86 (*quint.*, *J* = 6.8, 2 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 136.55; 136.24; 136.14; 135.86; 132.41; 130.38; 128.91; 127.09; 127.06; 126.47; 21.69; 56.39; 54.81; 25.79. FAB-MS (pos.): 623 (20, MH^+), 166 (15), 124 (12). HR-MS: 623.249400 ($C_{47}H_{31}N_2^+$; calc. 623.248734).

Data of **13**: M.p. 250° (dec.). R_f (CH_2Cl_2/MeOH 10 :1) 0.14. UV ($c = 1.1 \cdot 10^{-5}$ M $CHCl_3$): 258 (96500), 293 (43300). ^{1}H-NMR (400 MHz, $CDCl_3$): 7.74 (*d*, *J* = 8.8, 4 H); 7.72 (*s*, 4 H); 7.70 (*d*, *J* = 8.8, 4 H); 7.39 (*s*, 4 H); 4.38 (*d*, *J* = 14.4, 4 H); 3.74 (*d*, *J* = 14.4, 4 H); 2.55 (*s*, 4 H); 1.60 (*s*, 4 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 136.55; 136.37; 136.17; 135.85; 132.45; 130.38; 129.00; 127.10; 127.05; 126.47; 121.57; 56.99; 56.33; 25.46. FAB-MS (pos.): 637 (100, MH^+), 346 (85), 329 (22), 305 (30), 288 (47), 277 (80). HR-MS: 623.249400 ($C_{47}H_{31}N_2^+$; calc. 623.248734).

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REFERENCES

[1] F. Vögtle, 'Supramolecular Chemistry', John Wiley, New York, 1993.
[2] J.-M. Lehn, 'Supramolecular Chemistry', VCH, Weinheim 1994.
[3] L. T. Scott, *Pure Appl. Chem*. **1996**, *68*, 291.
[4] J. S. Siegel, T. J. Seiders, *Chem. Brit*. **1995**, *31*, 313.
[5] A. D. Hirsch, 'The Chemistry of the Fullerenes', G. Thieme Verlag, Stuttgart-New York, 1994.
[6] P. W. Rabideau, A. Sygula, *Acc. Chem. Res.* **1996**, *29*, 235.
[7] T. J. Seiders, E. L. Elliott, G. H. Grube, J. S. Siegel, *J. Am. Chem. Soc*. **1999**, *121*, 7804.
[8] A. H. Abdourazak, A. Sygula, P. W. Rabideau, *J. Am. Chem. Soc*. **1993**, *115*, 3010.
[9] A. Sygula, P. W. Rabideau, *J. Am. Chem. Soc*. **1999**, *121*, 7800.
[10] M. Maggini, G. Scorrano, M. Prato, *J. Am. Chem. Soc*. **1993**, *115*, 9798.
[11] M. Maggini, G. Scorrano, A. Bianco, C. Toniolo, R. P. Sijbesma, F. Wudl, M. Prato, *J. Chem. Soc., Chem. Commun.* **1994**, 305.
[12] P. Pfeiffer, K. Quehl, *Ber. Deutsch. Chem. Ges.* **1931**, *64*, 2667.
[13] T. J. Seiders, K. K. Baldridge, G. H. Grube, J. S. Siegel, *J. Am. Chem. Soc.*, in press.
[14] T. J. Seiders, K. K. Baldridge, E. L. Elliott, G. H. Grube, J. S. Siegel, *J. Am. Chem. Soc.* **1999**, *121*, 7439.
[15] T. J. Seiders, K. K. Baldridge, J. S. Siegel, *J. Am. Chem. Soc*. **1996**, *118*, 2754.
[16] A. Borchardt, K. K. Baldridge, A. Fuchicello, K. Kilway, J. S. Siegel, *J. Am. Chem. Soc*. **1992**, *114*, 1921.
[17] L. T. Scott, M. M. Hashemi, M. S. Bratcher, *J. Am. Chem. Soc*. **1992**, *114*, 1920.
[18] A. Sygula, P. W. Rabideau, *Theochem, J. Mol. Struct*. **1995**, *333*, 215.
[19] P. U. Biedermann, S. Pogodin, I. Agranat, *J. Org. Chem*. **1999**, *64*, 3655.
[20] J. Sandström, 'Dynamic NMR Spectroscopy', Academic Press, New York, 1982.
[21] W. Reid, J. Grabosch, *Chem. Ber*. **1958**, *91*, 2485.
[22] M. Prato, M. Maggini, *Acc. Chem. Res.* **1998**, *31*, 519.
[23] C. L. Perrin, M. A. Fabian, K. B. Armstrong, *J. Org. Chem*. **1994**, *59*, 5246.
[24] M. A. Fabian, C. L. Perrin, M. L. Sinnott, *J. Am. Chem. Soc*. **1994**, *116*, 8398.
[25] H. K. Hall, *J. Am. Chem. Soc*. **1957**, *79*, 5441.
[26] S. J. Broderius, M. D. Kahl, M. D. Hoglund, *Environ. Toxicol. Chem*. **1995**, 1591.
[27] A. I. Meyers, F. X. Taveres, *J. Org. Chem*. **1996**, *61*, 8207.

[28] M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis, J. A. Montgomery, *J. Comput. Chem*. **1993**, *14*, 1347.
[29] M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. DeFrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, Gaussian, Inc., Pittsburgh, PA 1994.
[30] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.
[31] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.
[32] B. Miehlich, A. Savin, H. Stoll, H. Preuss, *Chem. Phys. Lett*. **1989**, *157*, 200.
[33] C. Moller, M. S. Plesset, *Phys. Rev.* **1934**, *46*, 618.
[34] T. H. Dunning, Jr., P. J. Hay, 'Modern Theoretical Chemistry', Plenum, New York, 1976.
[35] T. Koopmans, *Physica* **1934**, *1*, 104.
[36] J. Almlof, B. Roos, U. Wahlgren, H. Johansen, *J. Electron. Spectrosc. Relat. Phenom.* **1973**, *2*, 51.
[37] K. D. Jordan, M. N. Paddon-Row, *J. Phys. Chem*. **1992**, *96*, 1188.
[38] SDSC, SDSC, San Diego, 1997.
[39] K. K. Baldridge, J. P. Greenberg, *J. Mol. Graphics* **1995**, *13*, 63.
[40] K. K. Baldridge, A. Klamt, *J. Chem. Phys*. **1997**, *106*, 6622.
[41] V. Barone, M. Cossi, *J. Phys. Chem. A* **1998**, *102*, 1995.

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