Hetero Diels–Alder Reactions with a Dicationic Urea Azine Derived Azo Dienophile and Their Use for the Synthesis of an Electron-Rich Pentacene

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1. Experimental Procedures

General experimental details

If not otherwise stated, all synthetic work was carried out under an inert-gas atmosphere using the Schlenk technique. The used chemicals were obtained from common companies (Sigma-Aldrich, Acros Organics, Alfa Aesar, abc GmbH and TCI (pentacene 99.999%, tetracene >97%)). Solvents were dried with an MBraun Solvent Purification System, degassed by three freeze-pump-thaw cycles and stored over molecular sieves prior to their use. Elemental analysis was carried out at the Microanalytical Laboratory of the University of Heidelberg. NMR spectra were recorded with Bruker DPX 200 (also VT-NMR), Bruker Avance II 400 or Bruker Avance III 600 spectrometers. HR-ESI spectra were recorded with a Bruker ApexQe hybrid 9.4 T FT-ICR spectrometer. IR spectroscopic measurements were performed on an FT-IR Biorad Merlin Excalibur FT 300 spectrometer. UV/Vis measurements were carried out on a Cary 5000 spectrometer. CV measurements were carried out at a Metrohm Autolab PGSTAT 204 potentiostat/galvanostat with an Ag/AgCl reference electrode. The curves were recorded at room temperature, CH2Cl2 or MeCN were used as solvent for the individual compounds (c = 10⁻³ M), whereas nBuN(PF6) (electrochemical grade (≥99.0%), Fluka) was employed as supporting electrolyte (c = 0.1 M). X-band EPR spectra were measured at room-temperature in a glass capillary with a Bruker ESP 300 E.

X-ray Crystallographic Study

Full shells of intensity data were collected at low temperature with a Nonius Kappa CCD diffractometer (Mo-Kα radiation, sealed X-ray tube, graphite monochromator, compound 2(BF₄)₂) and Bruker D8 Venture, dual source (Mo- or Cu-Kα radiation, microfocus X-ray tube, Photon III detector, compounds 3(BF₄)₂, 4(BF₄)₂, 5(BF₄)₂, 7(2H)(OTf)₂, and 8). Data were processed with the standard Nonius and Bruker (SAINT, APEX3) software package. Multiscan absorption correction was applied using the SADABS program. The structures were solved by intrinsic phasing and refined using the SHELXTL software package (Version 2014/6 and 2018/3). Graphical handling of the structural data during solution and refinement were performed with OLEX2. All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms bound to carbon were input at calculated positions and refined with a riding model. Hydrogen atoms bound to nitrogen were located in difference Fourier syntheses and refined, either fully or with appropriate distance and/or symmetry.

Due to disorder and fractional occupancy, electron density attributed to solvent of crystallization (Acetonitrile) was removed from the structure of 2(BF₄)₂ with the BYPASS procedure, as implemented in PLATON (squeeze/hybrid). Partial structure factors from the solvent masks were included in the refinement as separate contributions to Fcalc.

Crystallographic data for the structures reported in this paper have been deposited in the Cambridge Crystallographic Data Centre (see Chap. 11 for CCDC No.) These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Structures are visualized with ORTEP III.

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SUPPORTING INFORMATION

Details of quantum chemical calculations
Quantum-chemical (DFT) calculations were performed with the 7.3.1 suite of the TURBOMOLE program[9] using the B3LYP functional[10] together with the def2-TZVP basis set.[11] The RI (resolution identity) approximation[12] and multipole accelerated RI-J[13] was applied for structure optimization. All structures are stationary points on the energy potential surface as confirmed by frequency computations.[14] For the calculation of the thermodynamic properties unscaled harmonic vibrational frequencies were used. Time-dependent functional theory (TD-DFT) computations were performed to obtain the electronic excitations.[15] The excitation energies for the first 40 states were calculated. Dispersion was included by the DFT-D3[16] approach developed by Grimme and co-workers. In the calculations of free Gibbs energies, the solvent effect was considered with the conductor-like screening model (COSMO)[17] by means of single-point calculations (εs = 37.50 for CH3CN). The deviations between experimentally derived and calculated structures were analyzed with the program aRMSD[18] using default settings. Orbital visualization relied on the IboView program,[19] and the visualization of the optimized structures on the mercury program.[20]

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2. Experimental Details and analytical data for all compounds

Synthesis of the Diels-Alder dienophile 1(BF₄)₂

Using an upscaled, slightly modified procedure we achieved higher yields compared with the previously published procedure,[¹] 1,2-bis(1,3-dimethylimidazolidin-2-ylidene)-hydrazine[¹] (750 mg, 3.34 mmol, 1 eq.) and 1.00 g of NOBF₄ (1.00 g, 8.69 mmol, 2.6 eq.) are mixed in a Schlenk tube and dissolved in acetonitrile (30 mL), resulting in an immediate colour change to red-brown. While stirring, the reaction vessel is evacuated numerous times (at least 8 times) until the solvent started to boil and then purged with Ar to remove traces of NO. Then, the reaction mixture is stirred 16 h under slightly reduced pressure. Subsequently, all volatiles are removed in vacuo and the residue is dissolved in acetonitrile (8 mL) and crystallized by diffusion of diethyl ether (30 mL) from the gas-phase into the solution. The product 1(BF₄)₂ is obtained as red needles (1.24 g, 3.11 mmol, 93%).

¹H NMR (199.87 MHz, CD₃CN, 298 K): δ = 4.13 (s, 8 H, CH₂), 3.15 (s, 12 H, CH₃) ppm.
Further analytical data can be found in the literature.[²]

General procedure for the dicationic hetero Diels-Alder reaction of 1(BF₄)₂ with different dienes

The dicationic hetero Diels-Alder reaction is carried out by adding the dienophile 1(BF₄)₂ (1 eq.) and corresponding diene (1 eq.) in a Schlenk tube. After the addition of acetonitrile, the reaction mixture is stirred for the given reaction time (reaction progress can be followed by decolorization of the red reaction mixture). After the work-up, XRD suitable single crystals are grown.

2,3-Dimethylbutadiene Diels-Alder product, 2(BF₄)₂

The reaction is carried out by the general procedure with 1(BF₄)₂ (56 mg, 141 µmol, 1 eq.) and 2,3-dimethylbutadiene (16 µl, 141 µmol, 1 eq.) in MeCN (3 mL) for 10 min. Subsequently all volatiles are removed in vacuo and the residue is washed with Et₂O (3x3 mL) giving the title compound as a pale-white powder (59 mg, 123 µmol, 87%). XRD suitable single crystals are obtained by diffusion of Et₂O from the gas-phase into a MeCN solution.
**SUPPORTING INFORMATION**

**1H NMR** (399.89 MHz, CD$_2$CN, 294 K): $\delta = 3.97$ (4 H, bs, DA-bridge-CH$_2$), 3.78 (8 H, CH$_3$-gua.), 3.04 (s, 12 H, CH$_3$-gua.), 1.71 (bs, 6 H, CH$_2$-diene) ppm.

**13C{[H] NMR** (100.55 MHz, CD$_2$CN, 295 K): $\delta =$ 161.70 (C$_{\text{gua.}}$), 122.84 (C$_{\text{dienen.}}$), 53.55 (CH$_2$-DA-bridge), 51.13 (CH$_2$-gua), 36.43 (CH$_3$-gua), 15.57 (CH$_3$-diene) ppm.

**MS** (ESI$^+$, MeCN): m/z = 153.12 (100%, [M$-$BF$_4$]$^+$).

**Elemental Analysis** (C$_{38}$H$_{68}$B$_3$F$_6$N$_6$): MEW: 840.07 g/mol; calcd. C 40.03, H 6.30, N 17.51; found C 39.50, H 5.79, N 18.01

**Cyclopentadiene Diels-Alder product, 3(BF$_4$)$_2$**

The reaction is carried out by the general procedure with 1(BF$_4$)$_2$ (61 mg, 153.3 µmol, 1 eq.) and freshly distilled cyclopentadiene (13 µL, 153.3 µmol, 1 eq.) in MeCN (3 mL) for 5 min. Subsequently all volatiles are removed in vacuo and the residue is washed with Et$_2$O (3x3 mL) giving the title compound as a pale-yellowish powder (55 mg, 119 µmol, 77%). XRD suitable single crystals are obtained by diffusion of Et$_2$O from the gas-phase into a MeCN solution.

**1H NMR** (399.89 MHz, CD$_2$CN, 294 K): $\delta =$ 6.91-6.84 (2 H, m, RHC=CHR), 5.28-5.26 (m, 1 H, CH$_{\text{DA-bridge}}$), 5.23-5.22 (m, 1 H, CH$_{\text{dienen.}}$), 3.93-3.83 (m, 4 H, CH$_2$-gua.), 3.67-3.61 (m, 4 H, CH$_2$-gua.), 3.15 (s, 3 H, CH$_3$-gua.), 3.12 (bs, 6 H, CH$_3$-gua.), 2.91 (s, 3 H, CH$_3$-gua.), 2.06-1.98 (m, 2 H, CH$_2$-diene) ppm.

**13C{[H] NMR** (100.55 MHz, CD$_2$CN, 295 K): $\delta =$ 160.04 (C$_{\text{gua.}}$), 159.69 (C$_{\text{gua.}}$), 140.86 (RCH=CHR), 137.74 (RCH=CHR), 75.82 (CH$_{\text{DA-bridge}}$), 72.32 (CH$_{\text{dienen.}}$), 52.55 (CH$_2$-gua.), 49.57 (CH$_2$-gua.), 49.38 (CH$_2$-gua.), 36.60 (CH$_3$-gua.), 35.59 (CH$_3$-gua.) ppm.

**IR** (KBr): $\nu =$ 2949 (w), 2898 (w), 1611 (s), 1559 (s), 1457 (w), 1421 (m), 1379 (m), 1306 (m), 1055 (vs), 922 (w), 859 (m), 782 (w), 748 (w), 689 (w), 645 (w), 522 (m) cm$^{-1}$.

**HR-MS** (ESI$^+$, MeCN): m/z calcld for C$_{38}$H$_{68}$B$_3$F$_6$N$_6$ [M$-$BF$_4$]$^+$ = 377.2243, found m/z = 377.2243.

**Elemental Analysis** (C$_{38}$H$_{68}$B$_3$F$_6$N$_6$): MEW: 464.02 g/mol; calcld. C 38.83, H 5.56, N 18.11; found C 39.20, H 6.21, N 18.89.

**Tetracene Diels-Alder product, 4(BF$_4$)$_2$**

The reaction is carried out by the general procedure with 1(BF$_4$)$_2$ (400 mg, 1.01 mmol, 1 eq.) and tetracene (230 mg, 1.01 mmol, 1 eq.) under exclusion of light in MeCN (30 mL) for 36 h. Subsequently the reaction mixture is filtered under Ar, all volatiles are removed in vacuo from the filtrate and the residue is washed with Et$_2$O (3x3 mL) and ice cooled acetone (2x5 mL), yielding the title compound as an off-white powder (337 mg, 538 µmol, 53%). XRD suitable single crystals are obtained by diffusion of Et$_2$O from the gas-phase into a MeCN solution.
Pentacene Diels-Alder product 5(BF₄)₂

The reaction is carried out by the general procedure with 1(BF₄)₂ (400 mg, 1.01 mmol, 1 eq.) and pentacene (280 mg, 1.01 mmol, 1 eq.) under exclusion of light in MeCN (30 mL) for 72 h. Subsequently the reaction mixture is filtered under Ar, all volatiles are removed in vacuo from the filtrate, and the residue is washed with Et₂O (3×3 mL) and ice cooled acetone (2×5 mL), yielding the title compound as an off-white powder (527 mg, 780 μmol, 77%). XRD suitable single crystals are obtained by diffusion of Et₂O from the gas-phase into a MeCN solution.

** Elemental Analysis**  
CₙHₙBₙFₙNₙ,  

MW: 626.12 g/mol: calcd. C 53.71, H 5.15, N 13.42; found C 53.98, H 5.30, N 13.22.

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**Supporting Information**

**1H NMR** (399.89 MHz, CD₂CN, 295 K): δ = 8.24 (s, 1 H, CH₄rom.), 8.12 (s, 1 H, CH₄rom.), 7.99-7.96 (m, 2 H, CH₄rom.), 7.81-7.79 (m, 1 H, CH₄rom.), 7.73-7.71 (m, 1 H, CH₄rom.), 7.66-7.63 (m, 2 H, CH₄rom.), 7.52-7.50 (m, 2 H, CH₄rom.), 6.29 (s, 1 H, CH-DA-bridge), 6.28 (s, 1 H, CH-DA-bridge), 3.93-3.36 (m, 8 H, CH₂-gua.), 3.25 (s, 3 H, CH₃-gua.), 3.24 (s, 3 H, CH₂-gua.), 2.29 (s, 3 H, CH₃-gua.), 2.21 (s, 3 H, CH₃-gua.) ppm.

**13C{1H} NMR** (100.55 MHz, CD₂CN, 296 K): δ = 159.98 (C₉₃gua.), 137.98 (C₉₃rom.), 136.54 (C₉₃rom.), 133.93 (C₉₃rom.), 133.93 (C₉₃rom.), 133.51 (C₉₃rom.), 132.66 (C₉₃rom.), 131.07 (C₉₃rom.), 130.50 (C₉₃rom.), 129.70 (C₉₃rom.), 129.61 (C₉₃rom.), 128.94 (C₉₃rom.), 128.81 (C₉₃rom.), 126.71 (C₉₃rom.), 126.34 (C₉₃rom.), 125.67 (C₉₃rom.), 125.14 (C₉₃rom.), 66.08 (CH₃-DA), 51.93 (CH₂-gua.), 49.11 (CH₂-gua.), 35.75 (CH₃-gua.), 35.68 (CH₃-gua.), 35.56 (CH₃-gua.), 35.39 (CH₃-gua.) ppm.

**IR** (KBr): 3040 (sh), 2953 (w), 2895 (w), 1718 (m), 1611 (vs), 1558 (s), 1507 (w), 1477 (w), 1466 (w), 1457 (w), 1419 (w), 1411 (w), 1374 (m), 1308 (m), 1218 (w), 1056 (vs), 935 (w), 859 (w), 835 (w), 818 (w), 772 (m), 761 (m), 734 (w), 613 (w), 699 (w), 686 (w), 647 (w), 627 (w), 580 (w), 567 (w), 552 (w), 522 (w), 488 (w) cm⁻¹.

**HR-MS** (ESI⁺, MeCN): m/z calcd for C₉₃H₉₃BF₄N₉ [M–BF₄⁺]⁺ = 539.2712, found m/z = 539.2720.

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**1H NMR** (600.13 MHz, CD₂CN, 295 K): δ = 8.28 (s, 2 H, CH₄rom.), 8.18 (s, 2 H, CH₄rom.), 8.01-7.99 (m, 4 H, CH₄rom.), 7.67-7.63 (m, 4 H, CH₄rom.), 6.41 (s, 2 H, CH₂-DA-bridge), 3.96-3.90 (m, 2 H, CH₂-gua.), 3.86-3.80 (m, 2 H, CH₂-gua.), 3.66-3.61 (m, 2 H, CH₂-gua.), 3.45-3.40 (m, 2 H, CH₂-gua.), 3.29 (s, 6 H, CH₃-gua.), 2.26 (s, 6 H, CH₃-gua.) ppm.

**13C{1H} NMR** (150.90 MHz, CD₂CN, 296 K): δ = 159.95 (C₉₃gua.), 134.12 (C₉₃rom.), 133.83 (C₉₃rom.), 133.74 (C₉₃rom.), 132.60 (C₉₃rom.), 129.73 (C₉₃rom.), 129.64 (C₉₃rom.), 128.98 (C₉₃rom.), 128.85 (C₉₃rom.), 128.85 (C₉₃rom.), 126.34 (C₉₃rom.), 126.34 (C₉₃rom.), 125.22 (C₉₃rom.), 125.22 (C₉₃rom.), 66.12 (CH₃-DA), 51.98 (CH₂-gua.), 49.18 (CH₂-gua.), 35.83 (CH₃-gua.), 35.67 (CH₃-gua.) ppm.

**IR** (KBr): ν = 3030 (w), 2957 (w), 2892 (w), 1616 (vs), 1558 (s), 1505 (w), 1457 (w), 1411 (w), 1375 (m), 1309 (s), 1231 (w), 1168 (w), 1052 (vs), 896 (w), 861 (m), 846 (m), 771 (m), 761 (m), 751 (m), 728 (m), 691 (w), 646 (w), 587 (w), 568 (w), 559 (w), 545 (w), 522 (w), 489 (w), 478 (m) cm⁻¹.

**HR-MS** (ESI⁺, MeCN): m/z calcd for C₉₃H₉₃BF₄N₉ [M–BF₄⁺]⁺ = 589.2869, found m/z = 589.2868.

**Elemental Analysis** (C₉₃H₉₃BF₄N₉, MW: 676.27 g/mol): calcd. C 56.83, H 5.07, N 12.43; found C 56.23, H 5.25, N 12.97.

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**Wiley-VCH**
**SUPPORTING INFORMATION**

6,13-Bis(N,N'-dimethylthleneguanidinyl)-pentacene, 7

In a Schlenk tube, 5(BF$_4$)$_2$ (100 mg, 147.9 µmol, 1 eq.) and KOtBu (34 mg, 303.1 µmol, 2.05 eq.) are mixed. After addition of THF (4 mL) a green suspension formed, that is stirred for 22 h under exclusion of light. Subsequently the reaction mixture is filtered and the residue is dried. The raw product is washed under Ar with THF (3x4 mL). Then, it is suspended in DCM and washed with water (3x4 mL) (filtering under Ar) to remove KBF$_4$. Unfortunately, it is not possible to remove all KBF$_4$ due to its low solubility. Please note that the reaction does not work with LiOtBu in place for KOtBu, indicating that the formation of un-soluble KBF$_4$ might be an important driving force. The title compound is obtained as an emerald coloured powder (35 mg, 70 µmol, 47%)

**IR (KBr):** $\tilde{\nu}$ = 3046 (w), 2951 (w), 2845 (w), 1624 (vs), 1613 (vs), 1483 (m), 1431 (m), 1414 (m), 1383 (s), 1267 (m), 1236 (w), 1197 (w), 1135 (m), 1050 (m), 1011 (m), 993 (w), 955 (s), 877 (w), 792 (w), 700 (w), 621 (w), 514 (w), 466 (m) cm$^{-1}$

**UV-Vis (CH$_2$Cl$_2$, c = 8.353·10$^{-5}$ mol L$^{-1}$):** $\lambda_{\max}$ (ε, 10$^3$ L mol$^{-1}$ cm$^{-1}$) = 718 (3.3), 675 (2.98), 453 (4.1), 428 (2.0), 318 (11.8), 257 (11.4) nm.

**HR-MS (ESI$^+$, CH$_2$Cl$_2$):** m/z calcd for C$_{32}$H$_{32}$N$_6$+ [M+H]$^+$ = 501.2761, found m/z = 501.2762.

**Elemental Analysis (C$_{32}$H$_{32}$N$_6$·0.4 KBF$_4$, MW: 500.65 g/mol):** calcd. C 69.75, H 5.85, N 15.25; found C 70.19, H 6.06, N 14.66.

6,13-Bis(N,N'-dimethylethleneguanidinum)pentacene bistriflate/chloride, (7+2H)(OTf/Cl)$_2$

In a Schlenk tube 7 (15 mg, 30 µmol, 1 eq.) is suspended in THF (4 mL) under the absence of light trifluoromethanesulfonic acid (6 µL, 63 µmol, 2.1 eq.) is added. The reaction mixture immediately changes colour from a green suspension to a deep blue purple solution. It is stirred for a period of 5 min. Then all volatiles are removed _in vacuo_ and the residue is washed with Et$_2$O (2x3 mL). For the growth of XRD suitable single crystals, the purple residue is dissolved in MeCN (2.5 mL) and stored at −18 °C.

The reaction was also done with HCl (2 Molar solution in Et$_2$O, 20 µl, 2.1 eq) for this reaction and dissolved in MeCN. The reaction mixture was stirred for a period of 5 min. Then all volatiles are removed _in vacuo_ and the residue is washed with Et$_2$O (2x3 mL). The blue purple residue was used directly for UV-Vis measurements.

**UV-Vis (MeCN, c = 4.794·10$^{-5}$ mol L$^{-1}$):** $\lambda_{\max}$ (ε, 10$^3$ L mol$^{-1}$ cm$^{-1}$) = 609 (5.6), 561 (4.1), 521 (1.9), 432 (2.0), 407 (1.7), 302 (75.2), 265 (17.2), 253 (16.1), 226 (31.6), 205 (31.8) nm.
In a Schlenk tube, 7 (10 mg, 20 µmol, 1 eq.) and AgSbF₆ (14 mg, 40 µmol, 2.05 eq.) are mixed and MeCN (4 mL) is added under exclusion of light, resulting in an immediate color change to a yellow solution. After stirring for 2 h, the reaction mixture is filtered, and the solvent removed in vacuo. The yellow residue is dissolved in MeCN (0.5 mL) and crystals are obtained by diffusion of Et₂O (5 mL) from the gas-phase into this solution (8 mg, 8 µmol, 41%).

**¹H NMR** (600.13 MHz, CD₃CN, 293 K): δ = 8.67 (s, 4 H, CH₃rom.), 8.31-8.29 (m, 4 H, CH₃rom.), 7.91-7.89 (m, 4 H, CH₃rom.), 4.03 (s, 8 H, CH₂, gua.), 2.91 (s, 12 H, CH₃, gua.) ppm.

**¹³C(¹H) NMR** (150.90 MHz, CD₃CN, 293 K): δ = 167.41 (Cqₐrom.), 163.45 (Cqₐgu.), 133.76 (Cqₐrom.), 132.15 (Cqₐrom.), 131.50 (CH₃rom.), 128.63 (Cqₐrom.), 49.85 (CH₂gua.), 33.43 (CH₃gua.) ppm.

**IR** (KBr): ̃ν = 3031 (w), 2964 (w), 2943 (w), 2900 (w), 2817 (sh), 1685 (s), 1673 (s), 1617 (s), 1587 (s), 1546 (m), 1496 (w), 1481 (w), 1458 (m), 1466 (m), 1425 (w), 1410 (w), 1395 (m), 1375 (m), 1295 (s), 1285 (sh), 1206 (m), 1064 (m), 995 (m), 969 (m), 934 (m), 841 (w), 798 (w), 765 (m), 700 (w), 657 (vs), 627 (w), 473 (w) cm⁻¹.

**UV-Vis** (MeCN, c = 7.731·10⁻⁶ mol L⁻¹): λ_max (ε, 10² L mol⁻¹ cm⁻¹) = 419 (9.1), 312 (15.6), 224 (10.5), 214 (7.8) nm.

**HR-MS** (ESI⁺, MeCN): m/z calcd for C₃₂H₂₈N₆SbF₆⁺ [M–SbF₆]+ = 735.1625, found m/z = 735.1620; m/z calcd for C₃₂H₂₈N₆Sb₂F₁₂⁺ [M–2SbF₆]²⁺ = 250.1339, found m/z = 250.1340.

**Elemental Analysis** (C₃₂H₂₈N₆Sb₂F₁₂): calcd. C 39.54, H 3.32, N 8.64; found C 39.11, H 3.53, N 8.86.
3. NMR analysis of the DA products

The DA products were investigated by $^1$H, $^{13}$C NMR as well as 2D-NMR and $^1$H NOESY experiments to elucidate their structure in solution (see SI). The $^1$H NMR (400 MHz, $d_3$-MeCN) spectrum of the butadiene adduct 2(BF$_4$)$_2$ contains four singlet signals at $\delta = 3.97$ (4 H), 3.78 (8 H), 3.04 (12 H) and 1.71 (6 H) ppm. The first two downfield shifted signals are broadened and belong to the methylene bridge and guanidinyl ethylene backbone. Structural conformation is further confirmed by the $^1$H NOESY NMR showing correlation through space for the four guanidinyl CH$_3$ groups with the CH$_2$ ring atoms as well as with the guanidinyl ethylene backbone. Furthermore, the methyl groups attached to the six-membered ring show correlation through space with the CH$_2$ ring atoms, too. The signal broadening is caused by either rotation or inversion of the guanidinyl groups in solution which cannot be resolved on the NMR time scale, leading to similar chemical shifts for all CH$_3$ and CH$_2$ protons in the $^1$H NMR spectra.

The $^{13}$C NMR spectrum of 3(BF$_4$)$_2$ contains eleven signals from which nine arise from carbon atoms connected to protons. These carbons bound directly to protons are assigned with the aid of $^1$H-$^{13}$C HSQC spectra (see SI). All carbon atoms in the former cyclopentadiene moiety are chemically inequivalent, while for the guanidinyl moieties some carbon atoms are equivalent on the NMR time scale. For example, there are two quaternary carbon signals for the central guanidinyl carbons but only two instead of four signals for the connected methyl and the ethylene groups. The compound should therefore exhibit C$_1$ symmetry in solution and the urea azine moiety on top of the cyclopentene ring adopts a trans conformation as seen in the crystal structure. Chemical equivalence for the guanidinyl backbone (methyl groups and ethylene bridge) could be established through rotation about the CN azine-guanidine bond. Flipping inversion at the azine N atoms of the guanidinyl groups can probably be ruled out due to the inequivalence of the carbon signals of the two guanidinyl groups.

The $^1$H NMR spectrum of the pentacene-DA product 5(BF$_4$)$_2$ shows four signals for the twelve aromatic protons, one signal for the two CH-bridge atoms with a characteristic shift of 6.41 ppm and two signals for the four guanidinyl methyl groups, as well as two complex multiplets for the ethylene bridge of the guanidinyl moiety. The compound presumably exhibits C$_2$ symmetry in solution giving a structure in which the guanidinyl groups again adopt trans-conformation (as in the crystal structure), for which half of the atoms are chemically equivalent. Interestingly, from $^1$H NOESY NMR we find direct chemical exchange for the guanidinyl protons in which the methyl groups interconvert. Similar spectra are obtained for the tetracene adduct.
4. Room-temperature reversible hetero Diels-Alder reaction of $6(BF_4)_2$:

![Diagram]

**Figure 4.1.** $^1$H NMR spectra (199.87 MHz, CDCl$_3$:CD$_3$CN (1:1)) of the VT-NMR (temperature region −40 – 55 °C) experiment showing the reversible nature of the DA reaction with anthracene (A) and $1(BF_4)_2$ (with hexamethylbenzene (HMB) added as internal standard). At low temperatures, the equilibrium is on the side of the DA product $6(BF_4)_2$, and at higher temperatures it shifts towards the reactants, $1(BF_4)_2$ and anthracene. Note that only the major signals used for the integration are shown.

NMR Signals for the anthracene adduct (not isolated):

$^1$H NMR (199.87 MHz, CD$_3$CN:CDCl$_3$ 1:1, 298 K): $\delta$ = 7.74-7.63 (m, 4 H, CH$_{\text{arom}}$), 7.49-7.44 (m, 4 H, CH$_{\text{arom}}$. Note: signals are covered by anthracene), 6.13 (s, 2 H, CH$_{\text{DA-bridge}}$), 3.97-3.41 (m, 8 H, CH$_2$$_{\text{gua.}}$), 3.20 (s, 6 H, CH$_3$$_{\text{gua.}}$), 2.24 (s, 6 H, CH$_3$$_{\text{gua.}}$ ppm.

Estimation of the equilibrium constants (see Figure 4.1 and Table 4.1) relied on the law of mass conservation. Absolute concentrations in the equilibrium were estimated with the aid of the internal standard hexamethylbenzene (HMB c = 8.14 mM, 1 and anthracene at a concentration of 30 mM) by integration of respective peak signals for anthracene (A), the dienophile 1 and the Diels-Alder product 6. In order to obtain more accurate concentrations, integration and speciation was carried out with the MestreNova internal module Mnova qNMR. The peak areas were deconvoluted in cases where they overlapped with other signals (accuracy of integration ±5%, errors estimated by error convolution).
Table 4.1. Estimated equilibrium constants from the VT $^1$H NMR experiment.

| $T$ / °C | $K_{eq}$ [l/mol] | $\Delta K_{eq}$ [l/mol] | $\ln(K_{eq})$ | $\Delta \ln(K_{eq})$ |
|----------|------------------|-----------------------|----------------|-------------------|
| -40      | 79.92            | 9.78                  | 4.3810         | 0.1224            |
| -35      | 75.98            | 9.30                  | 4.3305         | 0.1224            |
| -25      | 68.50            | 8.38                  | 4.2269         | 0.1224            |
| -15      | 57.16            | 7.00                  | 4.0459         | 0.1224            |
| -5       | 47.86            | 5.86                  | 3.8684         | 0.1224            |
| +5       | 37.12            | 4.51                  | 3.6142         | 0.1224            |
| +15      | 26.40            | 3.23                  | 3.2734         | 0.1224            |
| +25      | 15.26            | 1.87                  | 2.7249         | 0.1224            |
| +35      | 10.37            | 1.27                  | 2.3384         | 0.1224            |
| +45      | 5.21             | 0.64                  | 1.6514         | 0.1224            |
| +55      | 2.73             | 0.33                  | 1.0045         | 0.1224            |

The different solubility of the diene and dienophile component used in our reactions might hamper the analysis over a wide temperature regime. Anthracene is only partially soluble in MeCN in concentrations required for an NMR experiment,[4] while the dicationic dienophile is completely dissolved. In less polar solvents the opposite behaviour is found. For estimation of the equilibrium constant we therefore used a mixture of CD$_2$CN:CDCl$_3$ (1:1) to which an internal standard (hexamethylbenzene, 8.14 mM) was added. Evaluation of the thermodynamic parameters relied on a Van’t Hoff plot ($\ln(K_{eq})$ vs. $1/T$). For the full temperature region from −40 to +55 °C, a linear fit proved to be inadequate. The Van’t Hoff plot is linear on the assumption that there is no temperature dependence of thermodynamic data was carried out for the full temperature region (−40−55 °C) with a polynomial fit assuming a non-linear Van’t Hoff temperature dependence. For the higher temperature region (25−55 °C) shown in the inset, a linear fit was used. Results of the polynomial fit: $\Delta H(298K) = −35.6 ± 19.0$ kJ mol$^{-1}$, $\Delta S(298K) = −97.1 ± 33.3$ J mol$^{-1}$ K$^{-1}$. Results of the linear fit: $\Delta H = −47 ± 5$ kJ mol$^{-1}$, $\Delta S = −136 ± 15$ J mol$^{-1}$ K$^{-1}$. Deviations from the linear behaviour could be caused, for example, by a temperature-dependent conformational change or secondary equilibria.
SUPPORTING INFORMATION

such as solubility. Analytical expressions for the temperature-dependence are usually based on the change of heat capacity during a reaction. Then, a polynomial fit is used to account for a non-constant reaction enthalpy (see Figure 4.2).

Fitting our NMR data with the quadratic function \( \ln K_{eq} = a + \frac{b}{T} + c \frac{1}{T^2} \) results in a standard reaction enthalpy \( \Delta H^0 = -35.6 \pm 19.0 \text{ J mol}^{-1} \text{ K}^{-1} \) and a standard reaction entropy \( \Delta S^0 = -97.1 \pm 33.3 \text{ J mol}^{-1} \text{ K}^{-1} \).

Alternatively, the thermodynamic data could be derived from a linear fit for the higher temperature region (+25 to +55 °C), yielding a reaction enthalpy \( \Delta H = -47 \pm 5 \text{ kJ mol}^{-1} \) and a reaction entropy \( \Delta S = -135 \pm 15 \text{ J mol}^{-1} \text{ K}^{-1} \).
Table 5.1. Selected structural parameters (bond lengths in Å, angles in °, α dihedral angle between the two guanidinyl planes, β dihedral angle between the planes of the two carbon sites of the diene in the DA compound) of the DA products as well as 1_red and 1(BF_4)_2. Averaged values are given in cases with two independent molecules in the unit cell or two bonds of the same type.

| Compound | a     | b     | c     | d     | e     | f     | g     | α     | β     |
|----------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 1_red    | 1.416(1) | 1.296(1) | 1.396(1) | -     | -     | -     | -     | -     | -     |
| 1(BF_4)_2| 1.259(3) | 1.399(2) | 1.333(2) | -     | -     | -     | -     | -     | -     |
| 2(BF_4)_2| 1.405(4) | 1.365(3) | 1.330(4) | 1.470(3) | 1.500(4) | -     | -     | 81    | -     |
| 3(BF_4)_2| 1.438(5) | 1.391(6) | 1.326(6) | 1.554(6) | 1.508(6) | 1.514(6) | 1.326(3) | 73    | 129   |
| 4(BF_4)_2| 1.447(2) | 1.390(2) | 1.325(2) | 1.528(2) | 1.504(2) | 1.512(2) | 1.401(2) | 76    | 128   |
| 5(BF_4)_2| 1.449(2) | 1.391(2) | 1.322(3) | 1.525(2) | 1.501(3) | 1.513(3) | 1.425(3) | 82    | 125   |
6. Cyclovoltammetric studies

Figure 6.1. Cyclic voltammograms recorded for the DA product $2(BF_4)_2$ in MeCN at variable scan speed in reductive direction (0.1 M, N($n$Bu)$_4$PF$_6$, Ag/AgCl reference electrode). Potentials given vs. Fc$^+/Fc$ (applied as external reference).

Figure 6.2. Cyclic voltammograms recorded for the DA product $5(BF_4)_2$ in MeCN at variable scan speed in reductive direction (0.1 M, N($n$Bu)$_4$PF$_6$, Ag/AgCl reference electrode). Potentials given vs. Fc$^+/Fc$ (applied as external reference). The wave marked by an asterisk is due to O$_2$ reduction.
Figure 6.3. Comparison between the cyclic voltammograms recorded for the DA product 5(BF₄)₂ in MeCN in oxidative direction (two consecutive scans) and neutral 1_red in DCM (0.1 M N(nBu)₄PF₆, Ag/AgCl reference electrode, measured at scan rates of 100 mV s⁻¹. The wave marked by an asterisk is due to O₂ reduction.

Figure 6.4. Cyclic voltammogram of 7 in DCM (0.1 M N(nBu)₄PF₆, scan speed 100 mV/s, Ag/AgCl reference electrode). Potentials given vs. Fc⁺/Fc (applied as external reference).

The electronic properties of compound 7 were studied by cyclic voltammetry in DCM (Figure 6.4). The voltammogram shows a single, quasi-reversible redox process at E₁/₂ = −0.65 V (E_Ox = −0.56 V and E_red = −0.73 V). From chemical oxidation of 7 with AgSbF₆ (1 eq.) in MeCN we were able to isolate yellow crystals showing a stoichiometry of two SbF₆⁻ anions per one bisguanidinyl-pentacene.
Therefore, we assume that the wave observed in the cyclic voltammogram belongs to a quasi-reversible two-electron redox process. The quasi-reversible nature indicates that there should be only a small structural change between the neutral and dicationic redox state.\[6\] This is in accordance with the DFT calculations showing only small changes for the critical parameters between the calculated structure of 7 and crystal structure of 8. No formation of a butterfly conformation was observed upon oxidation, and the acene moiety is only slightly twisted. A related compound, 1,4-bis-tetramethylguanidinyl-benzene, was investigated earlier by our group.\[7\] The CV spectra show one quasi-reversible two-electron redox process ($E_{1/2} = -0.18$ V vs. Fc/Fc' in DCM), $\Delta E = 180$ mV). The lower redox potential of 7 is in accordance with the more electron-rich acene bridge.
7. Titration of 7 with AgSbF₆

Figure 7.1. UV-Vis-NIR spectra recorded for the titration of 7 with AgSbF₆ (applied equivalents are given in the legend) in DCM. The spectrum of the solvent plus compound 7 was used as reference. The spectrum of compound 7 in DCM referenced to the solvent is included for comparison (dashed line). The asterisks highlight the bands due to the DCM stabilizer amylene. The photos illustrate the colour changes during the titration. The spectra point to oxidation in two one-electron steps, with intermediate formation of the open shell compound 7••.
Figure 7.2. UV-Vis-NIR spectra recorded for the titration of 7 with AgSbF₆ (equivalents are given in the legend) in DCM. The solvent spectrum is used as reference. The spectrum of 8 in MeCN is included for comparison (dashed line). Compound 8 was synthesised by oxidation with AgSbF₆ (2 eq.) and purified by crystallisation.

UV-Vis spectra recorded upon titration of 7 with AgSbF₆ in DCM indicate a two-step oxidation process (see Figure 7.1 and 7.2). Upon oxidation with 0.25 to 1.00 eq. of AgSbF₆ the p-band (718 nm) as well as the higher energy α-band (453 nm) of the neutral from vanished. Instead, several new bands in the region 350-650 nm and weak bands in the NIR region between 1250 and 1600 nm appeared. The colour of the solution changes from green to red-brown. Upon further oxidation with up to 2 eq. AgSbF₆, the shoulder at about 525 nm as well as the NIR bands disappeared in the UV-Vis spectra (in comparison with the spectra for 1.00 eq. AgSbF₆). The colour of the solution now changed from red to yellow. According to TD-DFT calculations for 7⁺, the lowest energy transition is located in the NIR region at 1337 nm, and the second lowest energy transition is located at 544 nm (see also Figure 7.2). The very broad absorption in the NIR might be composed of more than one band. The lower-energy band is tentatively assigned to a charge resonance (CR) band, originating from the class III or borderline class III/II mixed-valence (MV) system.[8] (Alternatively, it is due to an enlarged π-system resulting from dimer formation of neutral 7 with its radical monocation 7⁺.[9]) The second lowest energy transition is also in good accordance with the observed shoulder at 525 nm. All attempts to isolate a salt of the radical 7⁺ failed, underlining its instability towards disproportionation to the dicaticonic and neutral redox states. Nevertheless, the results argue for a two-step oxidation process (two one-electron steps) as also found for amino-tetracene and amino-anthracene derivatives.[8c,10] Differential pulse voltammetry showed for amino-tetracene and amino-anthracene derivatives that the observed quasi-reversible single wave voltammogram consists of two successive reversible one-electron oxidation steps with a minuscule potential difference of ΔE = 40 mV and ΔE = 60 mV, respectively.

In relation to our work we want to note the work by Ito et al. on the synthesis and redox properties of various diamino-acenes.[6,10] In summary these systems represent Wurster-type redox systems characterised by three distinct redox states. TMPD, the precursor to the radical denoted Wurster’s blue, is a well-known representative.[11] However as shown by Ito et al., by enlarging the π-system of the bridge between the two redox sites, the two step oxidation process is not necessarily preserved, as structural differences in the oxidised form might induce a change to a single two-electron process (with inverted oxidation potentials) and also might affect the electrochemical reversibility.

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8. EPR spectra

Figure 8.1. a) EPR spectrum (first derivative) of the reaction mixture of 7 and Ag(SbF$_6$) (0.5 eq.) in DCM. The spectrum was analysed with a low-pass filter (0.3 Hz, red line). b) Second derivative of the EPR signal. Spectrometer frequency $f = 9.637092$ GHz, $g = 2.0029$.

Figure 8.2. EPR spectrum of the filtrate of the reaction mixture of 5(BF$_4$)$_2$ and LDA (1 eq.) in THF-d$_8$. Spectrometer frequency $f = 9.634851$ GHz. The spectrum probably shows two paramagnetic species.
Further evidence for the presence of a radical form $7^+$ is provided by EPR experiments. The EPR spectrum of a solution containing 7 and 0.5 or 1.0 eq. of AgSbF$_6$ in DCM shows a broad paramagnetic signal ($g = 2.0029$) (see Figure 8.1). Hyperfine splitting is almost unresolved, but the free electron is expected to predominantly couple with two nitrogen cores adjacent to the pentacene moiety, therefore one would expect a quintet signal (not resolved). Interestingly investigation of the filtrate obtained from the reaction of the pentacene DA product 5 and LDA in THF shows a similar but better resolved paramagnetic signal ($g = 2.0020$) and a second signal ($g = 2.0150$) (Figure 8.2). Preparation of the EPR probe under air or measuring of the probe after about a day leads to vanishing of the second signal and broadening of the first signal ($g = 2.0029$) while the hfs is still visible (Figure 8.3). Observation of a paramagnetic signal for the reaction of $5$(BF$_4$)$_2$ with KOtBu/LDA to give 7 indicates oxidation to $7^+$, probably due to a competing redox reaction with 1 accompanied by retro Diels-Alder reaction:
9. Computational data

Ionic Diels-Alder reactions are quite rare in chemistry. They compromise reactions with positively or negatively charged ionic species as diene or dienophile component.\(^{[12]}\) The ionic nature is preserved along the reaction coordinate until formation of the ionic cycloadduct.\(^{[124]}\) In the last years several theoretical studies have been devoted to the mechanism of ionic DA reactions.\(^{[12a,13]}\) In these studies, different mechanisms have been proposed for DA reactions of non-charged and charged species. By inspection of the transition state structures, correlations between the experimental reaction rates and the global charge transfer were disclosed.\(^{[13a]}\) Recent work by Domingo et al. on the basis of favourable nucleophile/electrophilic interactions in the TS show that the rates of DA reactions (from neutral via polar to ionic DA) increases with polarity.\(^{[12b]}\) Therefore, ionic DA reactions proceed fast even at low temperatures. In a few cases the solvent effect on the transition states was included, showing significant influence on the energy of activation as well as regioselectivity predictions.\(^{[12d,13b]}\)

In our case the solvent effect is significant due to the charge of +2 of the dienophile. Therefore, some preliminary investigations were carried out on the influence of the solvent on the thermodynamics as well as kinetics of the herein described ionic DA reactions. Diene, dienophile and DA product were optimised at the B3LYP+D3/def2-TZVP level of theory and the solvent effect was estimated by single-point calculations with the conductor-like screening model (COSMO) for the solvent acetonitrile (\(\varepsilon_r = 37.5\)). The calculated thermodynamic data, collected in Table 9.1, indeed highlight the solvent effect on the reaction thermodynamics. Overall, they are less exothermic and less exergonic for \(\varepsilon_r = 37.5\) than for \(\varepsilon_r = 1\). These results are in line with the results of the studies of Domingo et al. on DA reactions with protonated imine derivatives and cyclopentadiene, showing that the separated reactants are preferentially stabilized due to larger localisation of the positive charge on the dienophile.\(^{[13b]}\) The calculations also explain the experimental result that no DA reaction occurs with the dienes furan and pyrrole. Additionally, they highlight that for anthracene, for which a chemical equilibrium is found at room temperature, the position of the equilibrium depends on the relative solvent permittivity (the solvent polarity).

| Diene          | B3LYP+D3/def2-TZVP +COSMO (sp) | B3LYP+D3/def2-TZVP |
|---------------|-------------------------------|-------------------|
|               | \(\Delta G\) | \(\Delta H\) | \(\Delta G\) | \(\Delta H\) |
| E-2,3-dimethylbutadiene including 2 \(\text{BF}_2^-\) | -75.4 | -143.5 | -112.4 | -180.5 |
| Z-2,3-dimethylbutadiene including 2 \(\text{BF}_2^-\) | -82.5 | -152.1 | -119.7 | -189.3 |
| furane        | 68.6 | -3.8  | 42.3  | -30.1 |
| pyrrol        | 114.5 | 40.1  | 70.2  | -4.2 |
| cyclopentadiene | -1  | -75.6 | -34.6 | -109.3 |
| anthracene    | 30.7 | -45   | -49.9 | -125.6 |
| tetracene     | 4.5  | -71.1 | -88.4 | -164.0 |
| pentacene     | -24.2 | -99.7 | -128.4 | -203.9 |

Table 9.1. Calculated \(\Delta G\) and \(\Delta H\) values for the DA reactions (values given in kJ mol\(^{-1}\)), with and without inclusion of the solvent effect (COSMO, \(\varepsilon_r = 37.5\) for MeCN). For the butadiene reaction the values were also calculated with optimised structures including the \(\text{BF}_2^-\) anions in the dienophile and DA product.

Qualitative information about the reaction kinetics could be derived from the Frontier Molecular Orbital (FMO) theory. According to the FMO theory (considering only electronic interactions between HOMO/LUMO in the rate-determining TS), the reaction rate of the DA reaction is proportional to the interaction energy of the HOMO and LUMO orbitals of diene and dienophile.\(^{[14]}\) The interaction energy depends on the degree of favourable orbital overlap as well as the energy difference between the frontier orbitals.\(^{[15]}\) For a normal electron demand DA reaction the HOMO of the nucleophilic diene and the LUMO of the electrophilic dienophile are of relevance.
Assuming that the orbital overlap for a given series of reactions is similar, the interaction energy only depends on the HOMO-LUMO gap. Hence, we compared the HOMO-LUMO gap between the dienophile 1 and the corresponding dienes with and without solvent effect (COSMO), and in addition tested the influence of an inclusion of the BF$_4^-$ anions for the DA reaction with 2,3-dimethylebutadiene (Figure 9.1). As expected, more electron rich dienes have higher HOMO energies, and the inclusion of the solvent effect for the neutral dienes only slightly alters the frontier orbital energies. On the other hand, the inclusion of the solvent effect raises the energies of both HOMO and LUMO of the doubly-charged dienophile significantly. The LUMO energy of the diene is now in the region where interaction with the diene HOMO is expected for the case of a normal electron-demand DA reaction. Interestingly, inclusion of the anions for the dienophile in the DFT calculations has a similar effect on the energy of the frontier MOs. Inclusion of the solvent effect for these salts again raises the HOMO and LUMO energies, but only slightly. Therefore, the COSMO structure of 1 can be considered as a good approximation (counterions/salts in frequency calculation are often problematic since they often have multiple minima structures on the PES). Qualitatively, the reaction rate is larger for cyclopentadiene than for butadiene. This experimental result could be explained within the framework of the FMO theory by the smaller HOMO-LUMO gap (diene/dienophile), in line with our basic theoretical analysis. Furthermore, one would expect the rate to increase with the size of the acene. We can say that for the best-soluble acene in this series, anthracene, the rate is high as the equilibrium quickly (<5 min) responds to temperature changes. However, one would expect the reactions with the larger acenes to be even faster. Here the poor solubility might be the limiting factor.

Another point is the competition between DA pathway and an electron transfers (redox) pathway. As the dienes become more electron rich an electron transfer might be favoured. The competing redox pathway is also influenced by the solvent as the LUMO energy of the dienophile depends on the solvent polarity.

**Figure 9.1.** HOMO and LUMO energies (B3LYP+D3/def2-TZVP) for the applied dienophile and dienes with and without inclusion of the solvent effect (COMSO, $\varepsilon_r = 37.5$ for MeCN). The impact of the two BF$_4^-$ anions on the orbital energies of the dienophile has also been considered (1 vs. 1(BF$_4$)$_2$). Note that butadiene stands for 2,3-dimethylebutadiene.
Figure 9.2. Frontier Kohn-Sham orbital energy levels for the ground state of $7$ at the B3LYP+D3/TZVP level of theory. The solid and dashed arrows represent the major contributions related to the lowest and next lowest vertical transitions calculated by TD-DFT. Data gives the calculated vertical transition energy and oscillator strength as well as the orbital contributions (squared “coefficient” of a single electron excitation from orbital i to orbital a) of the related excited state. Orbitals plotted at 80 % threshold.

Figure 9.3. Frontier Kohn-Sham orbital energy levels for the ground state of $7^\ast$ at the B3LYP+D3/TZVP level of theory.
Figure 9.4. Frontier Kohn-Sham orbital energy levels for the ground state of 8 at the B3LYP+D3/TZVP level of theory.
10. Structural comparison of 7

Figure 10.1. Comparison of the calculated structure of 7 (B3LYP+D3/TZVP) with the results obtained from XRD analysis for (7+2H)2+, plotted with the program aRMSD.

Figure 10.2. Molecular structures of (7+2H)2+(OTf)2 (a) and 8(SbF6)2 (b) (anions omitted). In case of (7+2H)2+(OTf)2 there are two molecules of MeCN per unit. All carbon-bound hydrogens are omitted for clarity. Displacement ellipsoids drawn at the 50% probability level.
The structure of neutral 7 was calculated at B3LYP+D3/TZVP level of theory. The comparison between the calculated structure of 7 and that obtained by SCXRD for (7+2H)$_2^+$ (see Figure 10.1) shows that both structures are similar, deviating only in some bond lengths. Interestingly in the protonated form the two guanidinyl groups are located in a plane almost perpendicular to the pentacene ring plane (see Figure 10.2a). In the oxidised form the guanidinyl groups are twisted about 90° (see Figure 10.2b). While we find a planar acene structure for the protonated form, the oxidised form shows a slightly twisted acene structure. Furthermore, the angle between the acene carbon and the guanidinyl group (\(\angle(C11-C1-N1)\)) is larger than 120°. These observations are in line with earlier studies by our group on the structural parameters of 1,4-bis(tetramethylguanidinyl)-benzene.\(^7\) For the oxidised form we also found a bent-twisted structure, in which the nitrogen atom establishes \(\pi\)-interactions with the carbon \(\pi\)-system as well as the CN$_2$ group of the guanidinyl group.
### Results of the crystal structure determinations

| Compound  | 2(BF$_4$)$_2$ | 3(BF$_4$)$_2$ | 4(BF$_4$)$_2$ | 5(BF$_4$)$_2$ |
|-----------|---------------|---------------|---------------|---------------|
| **CCDC No.** | 1982181 | 1982183 | 1982184 | 1982182 |
| **Formula** | C$_{32}$H$_{60}$B$_4$F$_{16}$N$_{12}$ | C$_{16}$H$_{27.5}$B$_2$F$_8$N$_{6.5}$ | C$_{56}$H$_{64}$B$_4$F$_{16}$N$_{12}$ | C$_{32}$H$_{34}$B$_2$F$_8$N$_6$ |
| $D_{calc}$ / g cm$^{-3}$ | 1.436 | 1.475 | 1.411 | 1.431 |
| μ/mm$^{-1}$ | 0.134 | 0.138 | 0.12 | 0.119 |
| **Formula Weight** | 960.16 | 484.56 | 1252.43 | 676.3 |
| **Colour** | colourless | clear colourless | clear light yellow | yellow |
| **Shape** | box shaped | block | block | [shape ?] |
| **Size/mm$^3$** | 0.50×0.30×0.20 | 0.20×0.14×0.08 | 0.58×0.23×0.20 | 0.44×0.33×0.18 |
| **T/K** | 120 | 100(2) | 100(2) | 120 |
| **Crystal System** | monoclinic | monoclinic | monoclinic | monoclinic |
| **Space Group** | $P2_1/c$ | $P2_1/n$ | $P2_1/c$ | $P2_1/n$ |
| $a$/Å | 24.350(5) | 10.5539(19) | 21.0879(8) | 12.4813(8) |
| $b$/Å | 13.873(3) | 14.733(2) | 17.9336(6) | 18.0987(9) |
| $c$/Å | 13.535(3) | 28.133(5) | 16.2002(6) | 14.5247(9) |
| α/° | 90 | 90 | 90 | 90 |
| β/° | 103.78(3) | 93.736(6) | 105.783(2) | 106.935(2) |
| γ/° | 90 | 90 | 90 | 90 |
| $V$/Å$^3$ | 4440.5(16) | 4365.2(13) | 5895.6(4) | 3138.8(3) |
| **Z** | 4 | 8 | 4 | 4 |
| **Z’** | 1 | 2 | 1 | 1 |
| **Wavelength/Å** | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| **Radiation type** | MoKα | MoKα | MoKα | Mo Kα |
| $\theta_{max}$ | 0.861 | 2.377 | 1.814 | 2.21 |
| $\theta_{max}$ | 28 | 27 | 28.5 | 28.78 |
| **Measured Refl’s.** | 78799 | 60381 | 296594 | 50507 |
| **Ind’t Refl’s** | 10716 | 9516 | 14910 | 8152 |
| **Refl’s with I > 2(I)** | 6149 | 5545 | 11590 | 5465 |
| $R_{int}$ | 0.0949 | 0.1277 | 0.0605 | 0.0771 |
| **Parameters** | 589 | 631 | 886 | 456 |
| **Restraints** | 0 | 85 | 194 | 6 |
| **Largest Peak** | 0.73 | 1.506 | 0.715 | 0.71 |
| **Deepest Hole** | -0.338 | -0.509 | -0.533 | -0.7208 |
| **GooF** | 1.055 | 1.048 | 1.02 | 1.0373 |
| **wR$_2$ (all data)** | 0.2461 | 0.2687 | 0.1463 | 0.1785 |
| **wR$_2$** | 0.2187 | 0.2349 | 0.1303 | 0.1589 |
| **R$_1$ (all data)** | 0.1508 | 0.1565 | 0.0684 | 0.0979 |
| **R$_{int}$** | 0.0885 | 0.0953 | 0.0518 | 0.0643 |
| **Compound** | \((7+2H)^2\)(OTf)₂ | **8** |
|------------|------------------|-----|
| **CCDC No.** | 1982185 | 1982186 |
| **Formula** | \(C_{38}H_{40}F_{6}N_{8}O_{6}S_{2}\) | \(C_{32}H_{32}F_{12}N_{6}Sb_{2}\) |
| \(D_{\text{calc}}/\text{g cm}^{-3}\) | 1.473 | 1.842 |
| \(\mu/\text{mm}^{-1}\) | 0.22 | 1.639 |
| **Formula Weight** | 882.9 | 972.13 |
| **Colour** | clear light red | clear light yellow |
| **Shape** | block | cube |
| **Size/mm³** | 0.16×0.10×0.08 | 0.19×0.15×0.14 |
| **T/K** | 100 | 100 |
| **Crystal System** | triclinic | monoclinic |
| **Space Group** | \(P-1\) | \(P2_1/n\) |
| \(a/Å\) | 7.557(3) | 9.3514(5) |
| \(b/Å\) | 10.293(3) | 12.1077(8) |
| \(c/Å\) | 12.890(5) | 15.4830(11) |
| \(\alpha^\circ\) | 85.709(14) | 90 |
| \(\beta^\circ\) | 87.404(11) | 90.690(3) |
| \(\gamma^\circ\) | 84.859(8) | 90 |
| \(V/Å³\) | 995.1(6) | 1752.92(19) |
| **Z** | 1 | 2 |
| **Z'** | 0.5 | 0.5 |
| **Wavelength/Å** | 0.71073 | 0.71073 |
| **Radiation type** | MoKα | MoKα |
| **\(\theta_{\text{max}}\)** | 1.992 | 2.135 |
| **\(\theta_{\text{max}}^\circ\)** | 28.498 | 30 |
| **Measured Refl's.** | 45312 | 56105 |
| **Ind't Refl's** | 5043 | 5108 |
| **Refl's with I > 2(I)** | 4088 | 4471 |
| **\(R_{\text{int}}\)** | 0.0594 | 0.0575 |
| **Parameters** | 278 | 237 |
| **Restraints** | 0 | 0 |
| **Largest Peak** | 0.426 | 0.578 |
| **Deepest Hole** | -0.44 | -0.601 |
| **GooF** | 1.053 | 1.068 |
| **\(wR_2\) (all data)** | 0.107 | 0.065 |
| **\(wR_2\)** | 0.0975 | 0.0618 |
| **\(R_1\) (all data)** | 0.057 | 0.0313 |
| **\(R_l\)** | 0.044 | 0.0244 |
12. 1D- and (selected) 2D-NMR spectra of the described compounds

2(BF₄)₂

399.89 MHz  
CD₃CN  
294.3 K  
1D

100.55 MHz  
CD₃CN  
295.2 K  
1D
SUPPORTING INFORMATION

4(BF₄)₂

399.89 MHz
CD3CN
295.1 K
1D

* marks traces of DCM, # marks traces of MeCN

100.55 MHz
CD3CN
295.5 K
1D

1D-DEPT-135

* marks traces of DCM, # marks traces of MeCN
$\text{SUPPORTING INFORMATION}$

5(BF$_4$)$_2$

600.13 MHz

CD$_3$CN

295.0 K

1D

150.90 MHz

CD$_3$CN

295.0 K

1D

1D-DEPT-135

1D
SUPPORTING INFORMATION

$8(\text{SbF}_6)_2$

600.13 MHz
CD$_3$CN
293.3 K
1D

150.90 MHz
CD$_3$CN
295.1 K
1D
13. HR-MS spectra

**HR-MS \(3(BF_4)_2\)**

**Analysis Info**
- **Analysis Name**: D:\data_2019\Himmel\03568_000001.d
- **Acquisition Date**: 06.08.2019 08:01:55
- **Method**: ESI pos HPlmas 205-1800
- **Sample Name**: MW_118_1
- **Comment**: Warr. AK-Himmel: MW_118_1 in ACN
- **Instrument**: ICR Apex-QqQ
- **Operator**: I.Mitch

**Acquisition Parameters**
- **Accumulations**: 16
- **Broadband Low Mass**: 173.2 m/z
- **Broadband High Mass**: 2500.0 m/z
- **Data Acquisition Size**: 2007/152

**Mass Spectrum Formula Report**
- **Analysis Info**: D:\data_2019\Himmel\03568_000001.d
- **Acquisition Date**: 06.08.2019 08:01:55
- **Comment**: Warr. AK-Himmel: MW 118_1 in ACN

---

**Figure Description**

- The HR-MS spectrum for \(3(BF_4)_2\) is shown with peaks at various m/z values.
- The mass spectrum formula report highlights specific peaks and their corresponding masses.

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**Table of Data**

| m/z | Mass, m/z | Ion Formula | m/z | err [ppm] | mSigma | rdb | e' | Conf | N-Rule |
|-----|-----------|-------------|-----|-----------|---------|-----|----|------|--------|
| 377.2243 | C15H26BF4N6 | 377.2243 | -0.2 | -2687.5 | 952.6 | 4.5 | even | ok |        |
| 377.2281 | | 378.2189 | 17.4 | 952.6 | 5.0 | ok |        |
| 378.2277 | | 377.2249 | 4.5 | 952.6 | 5.0 | ok |        |
HR-MS $5\text{(BF}_4\text{)}_2$

**Analysis Info**
- **Analysis Name**: D: data_2019_HimmeIscr34851_000001.d
- **Method**: ESI pos HPmix 200-1500
- **Sample Name**: MW_107.5
- **Comment**: Werr, AK Himmel: MW_107.5 in MeCN

**Acquisition Parameters**
- **Accumulations**: 15
- **Broadband Low Mass**: 179.3 m/z
- **Broadband High Mass**: 2933.0 m/z
- **Data Acquisition Size**: 2287132

| Parameter                  | Value             |
|----------------------------|-------------------|
| Collision Gas Flow Rate    | 0.5 L/sec         |
| Collision Energy           | 0.5 eV            |
| Linewidth Low m/z          | 1200.0 eV         |
| Q1 Resolution              | 5.0               |
| Q1 Mass                    | 200,000 m/z       |

**Mass Spectrum Formula Report**

**Analysis Info**
- **Analysis Name**: D: data_2019_HimmeIscr34851_000001.d
- **Comment**: Werr, AK Himmel: MW_107.5 in MeCN

**Intensities**

| Mass, m/z  | Ion Formula | m/z  | err [ppm] | mSigma | db | e | Conf | N-Rule |
|------------|-------------|------|-----------|--------|----|---|------|--------|
| 589.2868   | C32H5BF6N6O | 589.2860 | 2.0       | 41.7   | 21.0 | odd |       | ck     |
| 589.2866   | C32H5BF4N6  | 589.2860 | 0.2       | 43.5   | 17.5 | even|       | ck     |
| 589.2878   | C32H5BF2P3O2 | 589.2878 | 1.8       | 125.5  | 12.5 | even|       | ck     |
HR-MS of reaction 5(BF$_4$)$_2$ + 2eq KOtBu filtrate showing 7$^+$
HR-MS of reaction $5(BF_4)_2 + 2\text{eq KOtBu}$ residue showing $(7+H)^+$
HR-MS $8\text{(SbF}_6\text{)}_2$

**Analysis Info**
Analysis Name: Z:\Himmel\Ion37203_000001.d
Method: ESI pos H/1xix 200-1800
Sample Name: MW_157_1
Comment: Wavr, AK Himmel: MW_157_1 in MeCN

**Acquisition Parameters**
- Accumulations: 16
- Broadband Low Mass: 172.2 m/z
- Broadband High Mass: 2550.0 m/z
- Data Acquisition Rate: 2097152
- Collision Gas Flow Rate: 0.5 L/sec
- Collision Energy: 0.5 eV
- Collision Cell RF: 1200.0 V
- Q1 Resolution: 5.0
- Q1 Mass: 200.000 m/z

**Acquisition Date**: 16.01.2020 11:22:14
**Instrument**: ICR Apex-Qe
**Operator**: I.Misch

**Capillary Entrance**: 4200.0 V
**Calibration Date**: Tue Jan 14 02:13:10 2020
14. IR spectra

IR (KBr) $5(BF_4)_2$

IR (KBr) $3(BF_4)_2$
IR (KBr) $4(BF_4)_2$

IR (KBr) 7
IR (KBr) \(8(SbF_6)_2\)
15. Calculated (B3LYP+D3/def2-TZVP) minimum structures (xyz coordinates)

Optimised structure of $1^{2+}$

![Optimised structure of 1²⁺](image)

### Energy

Energy = -720.8569747584

### Coordinates

|   | X   | Y   | Z   |
|---|-----|-----|-----|
| N | -2.1463346 | -0.1859449 | 1.8484678 |
| C | -2.4026255 | -0.9787323 | 3.0690570 |
| C | -0.9852391 | -1.3997082 | 3.5039028 |
| N | -0.1525501 | -1.0404229 | 2.3281423 |
| C | -0.8876042 | -0.3397659 | 1.4831817 |
| N | -0.4488783 | 0.3183553 | 0.3049035 |
| N | 0.3541004 | -0.3240197 | -0.3860090 |
| C | 0.8183162 | 0.3444768 | -1.5502135 |
| N | 0.9883171 | -0.3674501 | -2.6475318 |
| C | 1.4304892 | 0.5211595 | -3.7424561 |
| C | 1.7559094 | 1.8339966 | -3.0030593 |
| N | 1.1779556 | 1.6102425 | -1.6535506 |
| C | 1.2718561 | 2.6578347 | -0.6408813 |
| C | 0.6154541 | -1.7577423 | -2.8926668 |
| C | -3.2300233 | 0.4596122 | 1.1129562 |
| C | 1.2828764 | -1.3071295 | 2.3440585 |
| H | -3.0408488 | -1.2776146 | 2.8175686 |
| H | -2.9138889 | -0.3635997 | 3.8083323 |
| H | -0.8976506 | -2.4661442 | 3.7053464 |
| H | -0.6243935 | -0.8457603 | 4.3723005 |
| H | 2.2928137 | 0.0863507 | -4.2459557 |
| H | 0.6199073 | 0.6294458 | -4.4655464 |
| H | 1.2972075 | 2.7085908 | -3.4603268 |
| H | 2.8282646 | 2.0095500 | -2.9010423 |
| H | 1.0266789 | 2.2737074 | 0.3433022 |
| H | 2.2901741 | 3.0483176 | -0.6346613 |
| H | 0.5808010 | 3.4647256 | -0.8879222 |
| H | 0.4525833 | -2.2719341 | -1.9492659 |
| H | -0.2928686 | -1.8002237 | -3.4969755 |
| H | 1.4266282 | -2.2497181 | -3.4339813 |
| H | -3.8084294 | 1.0649180 | 1.8085342 |
| H | -2.8231344 | 1.0968871 | 0.3324624 |
| H | -3.8820393 | -0.2955052 | 0.6694028 |
| H | 1.6831706 | -1.0009735 | 3.3110773 |
|   | 1.4585066 | -2.3744221 | 2.2056353 |
|---|-----------|------------|-----------|
| H |           |            |           |
| H | 1.7908446 | -0.7617619 | 1.5559731 |
Optimised structure of 1(BF$_4$)$_2$

Energy = -1570.411159623

Coordinates

F  -0.2424577  -1.1482498  9.2035895
F   -1.1764561  -1.9375864  11.1601861
F  -0.1384460   0.1235230  11.1185054
F   1.1169992   -1.7869951  10.9418862
B  -0.1345947  -1.2141544  10.6313702
F   0.2729458   3.9963930   7.1427424
F   1.2126528   4.7789364   5.1861772
F   0.1711287   2.7197191   5.2308804
F  -1.0842675   4.6327141   5.3995209
B   0.1683868   4.0587458   5.7146788
N   0.6014249   1.2741244  8.0628228
N   1.3892401   2.2698018  10.1523216
N   2.3892876   0.4706041   9.3399670
C   1.4245866   1.3557183   9.2037866
C   2.3201377   1.8819542  11.2260751
H   1.7382684   1.6359773  12.1142851
H   2.9979872   2.7080421  11.4424972
C   3.0340328   0.6399935  10.3461470
H   4.1061650   0.7879312  10.5091561
H   2.8531497   -0.2549999  11.2280280
C   0.4227387   3.3683500  10.3461470
H   0.1439724   3.7687387   9.3921427
H   0.9035542   4.1068842  10.9517772
H  -0.4538619   2.9531281  10.8743068
C   2.6755312  -0.6722835  8.4900787
H   2.2332432  -1.5668094  8.9264446
H   3.7584957  -0.7787299  8.4191584
H   2.2650859  -0.4982653  7.5000099
N  -0.5773115  -1.5721461  8.2791939
N  -1.3640913   0.5759176  6.1901788
N  -2.3619882   2.3779527  6.9982929
C  -1.3994256   1.4906882  7.1378040
C  -2.2914264   0.9652266  5.1138879
H  -1.7067484   1.2094333  4.2271582
H  -2.9702724   0.1404275  4.8957424
C  -3.0045170   2.2086575  5.6882040
H  -4.0771642   2.0625236  5.8266285
H  -2.8210749   3.1030269  5.0947968
C  -0.3987583  -0.4928174  5.9957557
|   |   |   |   |
|---|---|---|---|
| H | -0.1252476 | -0.9268088 | 6.9538632 |
| H | -0.8785653 | -1.2609663 | 5.3903721 |
| H | 0.4809140  | -0.1103566 | 5.4753845 |
| C | -2.6482286 | 3.5222063 | 7.8469898 |
| H | -2.2090766 | 4.4164053 | 7.4067791 |
| H | -3.7312349 | 3.6265766 | 7.9210310 |
| H | -2.2343233 | 3.3517421 | 8.8361622 |
Energy = -955.4949393961

Coordinates

C  0.2880279 -0.9873447  1.5910974
N -0.3518708  0.0646972  0.9941620
N  0.4210313  0.1364718 -0.4011266
C  0.6875736  0.4917527 -1.1204891
C -1.2440322  0.9679091  1.7498326
C -1.7719743  0.1285953 -0.9993233
C -2.5698205  1.2204057  1.0818749
C -2.8158401  0.8235392 -0.1656253
C -3.5216615  1.9556024  1.9825572
C -4.1114714  0.9867729 -0.9089512
N  1.7004007  1.2453217 -0.6793756
N  0.8941074  0.0830119 -2.3775193
N  0.8672440 -0.8921383  2.7933647
N  0.4469285 -2.2077050  1.0678145
C  2.0769982  0.7635540 -2.9393040
C  2.7887553  1.2583885 -1.6797922
C  1.3180871 -2.2242567  3.2407946
C  1.3402323 -3.0106455  1.9297317
C  0.1266199 -0.8288861 -3.2169657
C  1.7545149  2.1049896  0.4927355
C -0.2434618 -2.8136330 -0.0599406
C  1.0415115  0.2561249  3.6745297
H -0.7478195  1.9231326  1.9438226
H -1.4266383  0.4983088  2.7167199
H -2.0945366 -0.8962314 -1.2045334
H -1.6974979  0.6403053 -1.9591929
H -4.4016282  2.3177859  1.4596854
H -3.8552239  1.3103614  2.8029617
H -3.0313865  2.8226212  2.4353765
H -4.0085641  1.7220097 -1.7126949
H -4.4087801  0.0432992 -1.3759269
H -4.9284403  1.3020598 -0.2670670
H  1.7624509  1.5758947 -3.5988369
H  2.6732211  0.0572114 -3.5131831
H  3.1826184  2.2664084 -1.7872049
H  3.5975726  0.5964264 -1.3627048
H  0.6142080 -2.6312005  3.9707104
H  2.2989440 -2.1468275  3.7052381
H  0.9460945 -4.0186218  2.0365133
| H   | 2.3370038 | -3.0675486 | 1.4869126 |
|-----|-----------|------------|-----------|
| H   | 0.8234476 | -1.4714860 | -3.7542989|
| H   | -0.5258108| -1.4546778 | -2.6209827|
| H   | -0.4696475| -0.2774771 | -3.9468731|
| H   | 2.3854010 | 2.9598131  | 0.2571898 |
| H   | 0.7664901 | 2.4838287  | 0.7374538 |
| H   | 2.1873054 | 1.5880582  | 1.3490303 |
| H   | -0.3489239| -3.8782654 | 0.1395130 |
| H   | -1.2416708| -2.3994128 | -0.1671904|
| H   | 0.3198851 | -2.6946998 | -0.9853018|
| H   | 0.3223895 | 0.2294304  | 4.4958240 |
| H   | 2.0466526 | 0.2193060  | 4.0934944 |
| H   | 0.9309666 | 1.1867502  | 3.1320638 |
Optimised structure of the 2,3-dimethylbutadiene DA adduct including anions

Energy = -1805.036093096

Coordinates

F 12.9665556  7.3393433  4.2464863
F 11.5267196  5.5512583  4.0001593
F 11.1658842  7.4686041  2.8087618
F 10.8156101  7.4532530  5.0745249
B 11.6602969  6.9642147  4.0427308
F  4.4258908  8.6980106  7.4516292
F  5.3380085  9.8655549  5.7015407
F  3.2402361  9.5170699  5.4956750
F  3.5730791 10.7668041  6.8834847
B  4.1240736  9.6076965  6.3924370
N  7.9230211  7.6253530  4.3149326
N  8.6013893  5.3289883  4.3332528
N  8.5513953  6.3897769  2.3932420
N  7.1462065  7.4894529  5.4664249
N  5.2995882  6.2402521  6.2720147
N  5.1373317  7.0786800  4.2305033
C  8.4647662  8.9556184  4.0010928
H  7.7720603  9.5040024  3.3524198
H  9.3971936  8.7866819  3.4642450
C  8.7534550  9.7966605  5.215260
C  8.3454737  9.4512902  6.4264508
C  7.5945007  8.1767363  6.686465
H  8.2306219  7.5142402  7.2825080
H  6.6956789  8.4131384  7.2536496
C  9.5241733 11.0328625  4.8512557
H  9.6025163 11.7375881  5.6742914
H  9.0462665 11.5551118  4.0161316
H  10.5346756 10.7625582  4.5300318
C  8.5636295 10.2291856  7.6911566
H  9.2470219 11.0637772  7.5621143
H  8.9767348  9.5844888  8.4736186
H  7.6093886 10.6174395  8.0593088
C  8.3742820  6.4929854  3.7139598
C  8.9681734  4.3036765  3.3417587
H  8.1487800  3.5902535  3.2188643
H  9.8629495  3.7857595  3.6747420
C  9.2326503  5.1276598  2.0795783
H 10.2952105  5.3171253  1.9277364
H  8.7918864  4.6878817  1.1854940
| C     | 8.9649854 | 5.1584334  | 5.7319024 |
|------|-----------|------------|------------|
| H     | 9.2715121  | 6.1077532  | 6.1549098  |
| H     | 9.8358330  | 4.5074995  | 5.7727304  |
| H     | 8.1468226  | 4.7130552  | 6.2995783  |
| C     | 8.4520698  | 7.4138391  | 1.3720547  |
| H     | 7.7169761  | 8.1617848  | 1.6461117  |
| H     | 8.1286510  | 6.9389616  | 0.4455241  |
| H     | 9.4238511  | 7.8861586  | 1.2182649  |
| C     | 5.8914921  | 6.9849055  | 5.3316972  |
| C     | 3.8907714  | 6.0246775  | 5.9203916  |
| H     | 3.2667859  | 6.7270726  | 6.4729219  |
| H     | 3.6103849  | 4.9984680  | 6.1554669  |
| C     | 3.8922369  | 6.3130492  | 4.4175217  |
| H     | 3.9149606  | 5.4035863  | 3.8109613  |
| H     | 3.0458449  | 6.9294458  | 4.1286935  |
| C     | 5.7501844  | 5.9343482  | 7.6150631  |
| H     | 6.8324736  | 5.8925662  | 7.6586057  |
| H     | 5.3582966  | 4.9544282  | 7.883079   |
| H     | 5.3781842  | 6.6829385  | 8.3166929  |
| C     | 5.2077678  | 8.1296906  | 3.2284457  |
| H     | 5.7762315  | 8.9693006  | 3.6108070  |
| H     | 4.1971849  | 8.4942685  | 3.0568872  |
| H     | 5.6267406  | 7.7556187  | 2.2933255  |
Optimised structure of the furan DA adduct

Energy = -950.8586214174

Coordinates

C 0.5605697  0.2521804 -2.8969129
C 1.0486577 -0.9757012 -3.0514830
C 2.0525663 -1.1385726 -1.9348919
N 1.2555074 -1.2975845 -0.6289944
N 0.6875545  0.0224144 -0.4580669
C 1.2874434  0.7937349 -1.6775751
O 2.5377448  0.1852435 -1.7295418
C -0.6668600  0.0924668 -0.2098958
N -1.5894476  0.8621414 -0.2593338
N -1.1761777  1.2630430  0.1764655
C -2.6441527  1.1701814  0.2797070
C -2.8655005 -0.3456469  0.2807918
C 1.9971463 -1.7867034  0.4452046
N 2.4911205 -1.1251395  1.4837619
N 2.2450746 -3.0922211  0.5041042
C 3.0509839 -2.0898312  2.4601982
C 3.1297978 -3.3887761  1.6455541
C -1.4768136 -2.2659853 -0.6574567
C -0.4790998  2.5191622  0.4135151
C 1.8829537 -4.1235808 -0.4573668
C 2.5748281  0.3138959  1.7242434
H -0.2173346  0.7587117 -3.4473206
H 0.7789946 -1.7401658 -3.7632628
H 2.8482075 -1.8700538 -2.0113034
H 1.3413255  1.6608720 -1.4807018
H -2.9908149  1.6567733  1.1805850
H -3.1056969  1.6620240 -0.5883503
H -3.6913029 -0.6592055 -0.3603453
H -3.0390333 -0.7402277  1.2847401
H 2.3834103 -2.1609537  3.3204568
H 4.0251155 -1.7464561  2.8010546
H 2.7585773 -4.2550799  2.1899812
H 4.1380846 -3.6055776  1.2853979
H -0.9875196 -2.6316999  0.1125779
H -2.4858491 -2.6459925 -0.7927716
H -0.9428117 -2.3572567 -1.5972348
H -0.9470872  3.0197266  1.2599505
H 0.5623196  2.3293603  0.6592972
H -0.5415583  3.1796589 -0.4545891
|   |   |   |   |
|---|---|---|---|
| H | 2.7505563 | -4.4153042 | -1.0536952 |
| H | 1.5222784 | -4.9996652 | 0.0809598 |
| H | 1.0961494 | -3.7635667 | -1.1136766 |
| H | 1.6588142 | 0.6920425 | 2.1787290 |
| H | 3.398631 | 0.4824375 | 2.4145697 |
| H | 2.7908083 | 0.8419351 | 0.8013816 |
Optimised structure of the pyrrol DA adduct

Energy = -930.9885266317

Coordinates

C  -2.6916192  1.4020104  -0.5578612
C  -3.0601005  0.3956022  0.1093226
C  -2.1358423  0.2512168  1.3282621
N  -1.8520386  1.6437777  1.6485431
C  -1.5604819  2.0116809  0.2517674
N  -0.3520837  1.0897029  0.0635434
N  -0.7476186  -0.0995988  0.7584468
C   0.8713799  1.6384432  0.4370199
N   1.4531314  2.5115211  -0.3827696
N   1.6069072  1.3810378  1.5109288
C   2.6767157  3.0503297  0.2368291
C   2.9180509  2.0594542  1.3837703
C   0.9513710  3.0347372  -1.6444041
C   1.2729086  0.6231117  2.7146310
C  -0.5715466  -1.3096078  0.1216393
N  -0.6746823  -2.4383415  0.8247625
N  -0.2461811  -1.5384457 -1.1492501
C  -0.5615450  -3.6040664 -0.0700101
C   0.0414370  -2.9797460 -1.3326621
C  -0.9239815  -2.5994279  2.2501549
C  -0.1021229  -0.6113733 -2.2686661
H  -3.0426597  1.7646385 -1.5121560
H  -3.7850906  -0.4415926 -0.1676035
H  -2.3981413  -0.3773029  2.1697890
H  -1.2895504  3.0479135  0.0861260
H   2.4981662  4.0701720  0.5854720
H   3.4873455  3.0654245 -0.4892524
H   3.1710273  2.5520009  2.3199177
H   3.6910248  1.3237536  1.1522922
H   1.7689851  3.0694897 -2.3638839
H   0.1679945  2.3896665 -2.0315183
H   0.5597338  4.0464658 -1.5153183
H   1.4938214  -0.4370649  2.5859533
H   1.8891574  1.0075824  3.5247588
H   0.2302654  0.7727366  2.9739311
H  -1.5480254  -0.4049233 -0.2416811
H   0.0814534  -4.3584309  0.3791336
H  -0.4295150  -3.3375418 -2.2453907
H   1.1203425  -3.1332360 -1.4077845
|   |   |   |   |
|---|---|---|---|
| H | -0.3298660 | -3.4376080 | 2.6126544 |
| H | -0.6211009  | -1.7049134  | 2.7874745 |
| H | -1.9767294  | -2.8121768  | 2.4475761 |
| H | -0.1462307  | -1.1966126  | -3.1844017|
| H | -0.9149285  | 0.1061202   | -2.2824776|
| H | 0.8565749   | -0.0927313  | -2.2349632|
| H | -2.6858919  | 2.1124926   | 1.9930546 |
Optimised structure of the cyclopentadiene DA adduct

Energy = -914.9552903468

Coordinates
C  -2.5572164  1.0523063 -1.2540486
C  -2.9846626  0.0397038 -0.6166259
C  -2.2924353 -0.0536689  0.7373757
C  -2.2168425  1.4975311  1.0556163
C  -1.5991087  1.7560124 -0.3199855
N  -0.3491698  0.8635313 -0.2309615
N  -0.7995325  0.3165124  0.4437033
C   0.8408818  1.4230900  3.33 -0.1696331
C   1.4324217  2.3341182 -0.6060961
C   1.5691434  1.1414895  1.2517494
C   2.6252373  2.8767532  0.0667106
C   2.8749593  1.8346560  1.1619460
N   0.9527469  2.8461631 -1.8954876
N   1.2748324  0.2695400  2.3850802
N   0.0980481 -1.7874953 -1.2877870
C   0.5108089 -3.2082495 -1.3522444
C  -1.0361897  2.7656100  2.0133118
N   0.3264287 -0.9002498 -2.4252255
H  -2.7908409  1.3722125 -2.2587763
H  -3.6433363 -0.8123465 -0.9857879
H  -2.6545246 -0.7294870  1.5012384
H  -3.2017652  1.8801534  1.1823045
H  -1.5787573  1.6934468  1.9019480
H  -1.3177685  2.7778875 -0.5405510
H   2.4093305  3.8698314  0.4676503
H   3.4493083  2.9560799 -0.6396815
H   3.1228808  2.2831970  2.1219399
H   3.6552087  1.1183755  0.8944579
H   1.8606833  2.9431817 -2.5470256
H   0.2883130  2.1574658 -2.3528007
H   0.5274081  3.8294435 -1.7920700
H   1.9436006  0.5496379  3.1958282
H   0.2536099  0.4019663  2.7271664
H   1.4500610 -0.7788331  2.1398526
H  -1.1517043 -4.3427079 -0.4624822
H   0.3803843 -4.5127453  0.4126974
|   |   |   |   |
|---|---|---|---|
| H  | 0.2135799 | -3.6373927 | -2.3064274 |
| H  | 1.5964141 | -3.2819326 | -1.2550235 |
| H  | -0.4450606 | -3.5316017 | 2.5136716  |
| H  | -0.9060338 | -1.8261922 | 2.5431247  |
| H  | -2.0865218 | -3.0639866 | 2.0453795  |
| H  | 0.4443530  | -1.5242210 | -3.3083001 |
| H  | -0.5246123 | -0.2467656 | -2.5805694 |
| H  | 1.2350884  | -0.3108538 | -2.2951721 |
Optimised structure of the anthracene DA adduct

Energy = -1260.305320051

Coordinates

C   0.0051251  1.3794382  1.9557230
C   -0.7954149  0.2662796  2.2340507
C   -0.3549201 -0.9573098  1.4799269
C   1.1107635  -1.2174425  1.7359018
C   1.9035878  -0.1052359  1.4348972
C   1.0906226  1.0639760  0.9539496
C   1.6853758  -2.3959124  2.1778767
C   3.0720644  -2.4463375  2.3401521
C   3.8600409  -1.3380948  2.0484651
C   3.2787041  -0.1561413  1.5840480
C   -0.2582407  2.6034728  2.5444799
C   -1.3251508  2.7007543  3.4411896
C   -2.1159679  1.5922268  3.7239864
C   -1.8593027  0.3627593  3.1130807
N   0.3374223  0.5753181 -0.3079597
N   -0.4372028 -0.5901216 -0.0225068
N   -0.2751159  1.5528446 -1.0660563
N   -1.5749021  1.7661985 -1.2614766
N   0.4774124  2.4146277 -1.7556658
C   -1.7591714  2.7972852 -2.3052030
C   -0.3695756  3.4381624 -2.3892600
C   -2.7311997  1.2073163 -0.5731257
C   1.9256397  2.4691787 -1.8659445
C   -0.3223945 -1.6400856 -0.9112917
N   -1.3093734 -2.5361099 -0.9978583
N   0.6574612 -1.8999084 -1.7746628
C   0.2593971 -3.0159825 -2.6591834
C   -0.9293830 -3.6273489 -1.9095751
C   -2.5759484 -2.5635187 -0.2854836
C   1.9873814  -1.3153934 -1.8876791
H   -0.9668405 -1.8226998  1.6491177
H   1.6894089  1.9246065  0.6753740
H   1.0742597  -3.2578790  2.4169620
H   3.5355991  -3.3502411  2.7060387
H   4.9315752  -1.3886926  2.1893227
H   3.8950246  0.7065211  1.3613779
H   0.3617849  3.4668878  2.3352808
H   -1.5310681  3.6450279  3.9277730
H   -2.9322482  1.6802387  4.4286240
|   |   |   |   |
|---|---|---|---|
| H | -2.4751524 | -0.4996531 | 3.3381296 |
| H | -2.0656350 | 2.3263748 | -3.2420248 |
| H | -2.5304696 | 3.5003175 | -1.9987397 |
| H | -0.2998715 | 4.3773759 | -1.8352591 |
| H | -0.0436985 | 3.6116397 | -3.4131290 |
| H | -3.1729142 | 0.3941649 | -1.1515044 |
| H | -2.4604068 | 0.8660847 | 0.4181854 |
| H | -3.4722625 | 1.9983984 | -0.4677821 |
| H | 2.3297146 | 3.2913359 | -1.2702870 |
| H | 2.3631950 | 1.5333798 | -1.5336359 |
| H | 2.1954212 | 2.6350213 | -2.9089454 |
| H | 1.0883864 | -3.7107536 | -2.7740572 |
| H | -0.0139116 | -2.6290988 | -3.6438438 |
| H | -0.6587761 | -4.5172766 | -1.3362689 |
| H | -1.7625785 | -3.8741747 | -2.5649157 |
| H | -3.3728120 | -2.8052689 | -0.9888605 |
| H | -2.5644564 | -3.3253271 | 0.4977558 |
| H | -2.7791051 | -1.5936933 | 0.1569628 |
| H | 2.0151246 | -0.5607605 | -2.6754457 |
| H | 2.3021316 | -0.8908699 | -0.9426088 |
| H | 2.6819567 | -2.1125982 | -2.1484913 |
Optimised structure of the tetracene DA adduct

Energy = -1413.917524685

Coordinates
C  -3.3834309  -2.2591513   1.4794375
C  -2.9418978  -2.9759931   0.3720645
C  -1.7206876  -2.6697716  -0.2320723
C  -0.9521219  -1.6490635   0.3000298
C  -1.3989626  -0.9233328   1.4094915
C  -2.6142243  -1.2186972   2.0036361
C   0.3811063  -1.1544551  -0.2062714
C  -0.4293139   0.1453307   1.8269236
C   1.3862861  -1.1728658   0.9082100
C   0.9334642  -0.4592080   2.0491945
C   2.6101768  -1.7781814   0.9002427
C   3.4433527  -1.7049105   2.0923059
C   2.9898140  -0.9770952   3.1973260
C   1.7147424  -0.3488783   3.1630146
C   4.7080854  -2.3340726   2.0923059
C   5.4912150  -2.2502797   3.2163011
C   5.0447482  -1.5347511   4.3465466
C   3.8213165  -0.9117764   4.3378207
N  -0.2587828   1.0776058   0.5977590
N   0.1441372   0.3369889  -0.5556394
C  -0.5481375   0.5883016  -1.7213222
C   0.4060630   2.2637447   0.8301407
N   1.6004082   2.6536582   0.3890252
C   1.8190806   4.0748746   0.7315897
C   0.7434750   4.3314065   1.7926753
N  -0.1837827   3.2121384   1.5638817
N   0.0287918   0.3240141  -2.8972651
C  -0.9242303   0.5489184  -3.9956486
C  -2.0105225   1.3831063  -3.3079688
N  -1.7608367   1.1173317  -1.8754501
C   1.3651728  -0.1839286  -3.1574957
C  -2.8056009   1.3672576  -0.8912979
C  -1.5083425   3.2038668   2.1612046
C   2.6557281   1.8876792  -0.2609296
H  -4.3271736  -2.5141706   1.9430603
H  -3.5451889  -3.7846056  -0.0191353
H  -1.3750433  -3.2377654  -1.0874188
H  -2.9584237  -0.6653074   2.8689746
H   0.7197370  -1.6596652  -1.1047333
|   |   |   |   |
|---|---|---|---|
| H | -0.7792919 | 0.7481044 | 2.6583208 |
| H | 2.9549559 | -2.329989 | 0.0323057 |
| H | 3.3693758 | 0.1938994 | 4.0361188 |
| H | 5.0501384 | -2.890972 | 1.2283950 |
| H | 6.4560839 | -2.7395468 | 3.2420188 |
| H | 5.6718810 | -1.4831684 | 5.2269745 |
| H | 3.4778735 | -0.3703614 | 5.2109632 |
| H | 2.8287086 | 4.2123588 | 1.1122727 |
| H | 1.6921486 | 4.6954143 | -0.1584565 |
| H | 0.2273204 | 5.2794262 | 1.6530153 |
| H | 1.1342233 | 4.2919154 | 2.8123784 |
| H | -0.4361016 | 1.0783407 | -4.8117639 |
| H | -1.2962983 | -0.4074273 | -4.3710855 |
| H | -3.0168049 | 1.0667784 | -3.5733221 |
| H | -1.9141824 | 2.4523933 | -3.5098029 |
| H | 1.8086091 | 0.3869537 | -3.9733988 |
| H | 1.9859593 | -0.0764580 | -2.2739201 |
| H | 1.3305503 | -1.2358448 | -3.4512467 |
| H | -3.7639154 | 1.1375412 | -1.3549411 |
| H | -2.6848061 | 0.7213605 | -0.0305749 |
| H | -2.8108931 | 2.4150997 | -0.5865059 |
| H | -1.9828440 | 4.1692587 | 1.9848308 |
| H | -2.1169841 | 2.4250662 | 1.7133333 |
| H | -1.4470543 | 3.0414568 | 3.2400741 |
| H | 3.6110112 | 2.2386534 | 0.1268087 |
| H | 2.5651402 | 0.8338444 | -0.0282524 |
| H | 2.6413913 | 2.0450772 | -1.3407857 |
Optimised structure of the pentacene DA adduct

Energy = -1567.529256890

Coordinates:

C  -0.0903705  1.2451652  2.3462751
C  -0.8416288  0.0555602  2.5405724
C  -0.3115767 -1.0907453  1.7305759
C   1.1555766 -1.2830881  2.0138525
C   1.8985882 -0.0935726  1.7895931
C   1.0273243  1.0481460  1.3554645
C   1.7766072 -2.4339799  2.4061803
C   3.1819336 -2.4428542  2.6186843
C   3.9309057 -1.2407409  2.4000293
C   3.2521321  0.0682077  1.9725195
C  -0.4263538  2.3997698  2.9928795
C  -1.5265660  2.4126622  3.8926715
C  -2.2801195  1.2105170  4.0948117
C  -1.9123228  0.0338946  3.3887283
N   0.3246622  0.5889215  0.0483103
N  -0.3748512 -0.6416925  0.2446065
C  -0.3417436  1.5682416 -0.6558957
N  -1.6504961  1.7097006  0.0859886
N   0.3596194  2.5234473 -1.2741842
C  -1.8898782  2.7947007 -1.8333735
C  -0.5451069  3.5295841 -1.8510515
C  -2.7754379  1.0363569  0.2237226
C   1.8018187  2.6761505 -1.3594748
C  -0.1586184 -1.6271925 -0.6940825
N  -1.0752153 -2.5855539  0.8613345
N   0.8637596 -1.7724279 -1.5353056
C   0.5751637 -2.8649999 -2.4875682
C  -0.5891606 -3.5974607 -1.8118177
C  -2.3585066 -2.7363525 -1.978887
C   2.1540810 -1.0969061 -1.5673349
H  -0.8965844 -1.9988980  1.8308649
H   1.5798262  1.9558910  1.1371251
H   1.2101710 -3.3421610  2.5806922
H   3.8203549  0.8408140  1.8086727
H   0.1481597  3.0808363  2.8473885
H  -2.4828815 -0.8751801  3.5438734
H  -2.1529143  2.3704930 -2.8051642
H  -2.7097904  3.4232463 -1.4931616
H  -0.5456227  4.4315426 -1.2341061
| H     |  -0.2194657 |  3.7937912 | -2.8554839 |
|-------|-------------|------------|------------|
| H     |  -3.1654490 |  0.2430938 | -0.8638686 |
| H     |  -2.4901619 |  0.6398727 |  0.7428490 |
| H     |  -3.5622085 |  1.7732991 | -0.0680578 |
| H     |  2.1469873  |  3.4803081 | -0.7050357 |
| H     |  2.2938074  |  1.7496588 | -1.0817274 |
| H     |  2.0719120  |  2.970405  | -2.3853542 |
| H     |  1.4553034  | -3.4926189 | -2.6083203 |
| H     |  0.3051710  | -2.4485651 | -3.4608180 |
| H     | -0.2722319  | -4.4949736 | -1.2750097 |
| H     | -1.3809371  | -3.8681948 | -2.5078409 |
| H     | -2.3200821  | -3.5352127 |  0.5466529 |
| H     | -2.6423252  | -1.8070401 |  0.2854500 |
| H     | -3.1139808  | -2.9940665 | -0.9406822 |
| H     |  2.1618515  | -0.3096137 | -2.3230589 |
| H     |  2.4004267  | -0.6922497 | -0.5935161 |
| H     |  2.9117069  | -1.8345108 | -1.8285304 |
| C     |  5.3272447  | -1.2542068 |  2.6195766 |
| C     |  5.9574632  | -2.4001303 |  3.0360641 |
| C     |  5.2203249  | -3.5828275 |  3.2520288 |
| C     |  3.8630378  | -3.6043523 |  3.0480869 |
| H     |  5.8945706  | -0.3449672 |  2.4617714 |
| H     |  7.0261656  | -2.3991481 |  3.2060308 |
| H     |  5.7316242  | -4.4762477 |  3.5859323 |
| H     |  3.2986505  | -4.5122695 |  3.2232427 |
| C     | -3.3691148  |  1.2280447 |  4.9999180 |
| C     | -3.7008186  |  2.3779556 |  5.6678198 |
| C     | -2.9588820  |  3.5607286 |  5.4694166 |
| C     | -1.8955199  |  3.5783380 |  4.6015016 |
| H     | -3.9358127  |  0.3187863 |  5.1558473 |
| H     | -4.5332021  |  2.3809985 |  6.3592982 |
| H     | -3.2300131  |  4.4573587 |  6.0113177 |
| H     | -1.3224860  |  4.4863856 |  4.4580028 |
SUPPORTING INFORMATION

Optimised structure of 7

Energy = -1566.857582522

Coordinates

C  -6.655647 -0.3835151 -0.7450214
C  -6.4476255 -1.6501634 -0.1173060
C  -5.1957695 -2.0456994 0.2415409
C  -4.0598516 -1.2092934 0.0015106
C  -4.2712722 0.0762546 -0.6276662
C  -5.6051083 -0.4465546 -0.9899051
C  -2.7732314 -1.5874078 0.3482698
C  -1.6573337 -0.7595355 0.1166137
C  -1.8704247 0.5329952 -0.5049973
C  -3.1833909 0.9024784 -0.8569338
C  -0.354036 0.7380612 -0.3094193
C  -0.5244612 0.9866630 -0.3876906
C  -0.7808795 1.4023128 -0.738836
C  2.0523898 -0.6717349 0.5940706
C  3.1403810 0.1517169 0.3625367
C  2.9304638 1.4322232 -0.2765917
C  1.6449843 1.8080184 -0.6254137
C  4.4737999 -0.2164377 0.7294874
C  5.5249298 0.6109041 0.4798117
C  5.3183422 1.8733439 -0.1579136
C  4.0673356 2.2663447 -0.5214661
N  -0.9976784 2.6079505 -1.3974312
N  -0.1791405 -2.3909330 1.1254435
C  -0.9792977 3.7725708 -0.8748001
C  0.3070921 -3.4606980 0.6264524
N  0.4843246 -4.6025702 1.3987329
C  1.3290609 -5.5457743 0.6887662
N  -1.1548124 4.9142409 -1.6477798
C  -0.7780258 6.0867073 -0.8792484
C  1.0430848 -5.1728848 -0.7607466
N  0.7563623 -3.7459273 -0.6584225
C  -1.0444476 5.6113479 0.5437246
N  -0.7858844 4.1790191 0.4410976
C  -1.1603404 3.3625347 1.5824368
C  -0.8919910 4.8849340 -3.0687342
C  0.2221744 -3.0984666 -1.8437456
C  0.5845654 -4.5063066 2.8373830
H  -7.6597770 -0.0891517 -1.0245413
### SUPPORTING INFORMATION

| H     | -7.2978471 | -2.2944136 | 0.0704905 |
|-------|------------|------------|-----------|
| H     | -5.0363755 | -3.0065149 | 0.7178279 |
|       | -5.7614887 | 1.4079835  | -1.4659265|
|       | -2.6102797 | -2.5448494 | 0.8257591 |
|       | -3.3350666 | 1.8620313  | -1.338674 |
|       | 2.2130541  | -1.6262305 | 1.0766272 |
|       | 1.4932166  | 2.7641209  | -1.107656 |
|       | 4.6293640  | -1.1745855 | 1.2125061 |
|       | 6.5286661  | 0.3181799  | 0.7626578 |
|       | 6.1691035  | 2.5158497  | -0.3490852|
|       | 3.9092376  | 3.2239742  | -1.0047081|
|       | 2.3912222  | -5.3944382 | 0.9348253 |
|       | 1.0642885  | -6.5771490 | 0.9261971 |
|       | 0.2851127  | 6.3333175  | -1.0223432|
|       | -1.3739027 | 6.9567220  | -1.1589626|
|       | 0.1702650  | -5.7216338 | -1.1429280|
|       | 1.8866969  | -5.3561200 | -1.4275017|
|       | -2.0881247 | 5.8015518  | 0.8326906 |
|       | -0.3902360 | 6.0756037  | 1.2828859 |
|       | -0.7746941 | 3.830581   | 2.4849733 |
|       | -2.2491284 | 3.2629740  | 1.6752497 |
|       | -0.7250365 | 2.3714823  | 1.5083001 |
|       | -1.4013724 | 5.7228971  | -3.5474059|
|       | 0.1826560  | 4.9544801  | -3.2899794|
|       | -1.267566  | 3.9512054  | -3.4799432|
|       | -0.8157417 | -3.3953031 | -2.0401582|
|       | 0.2631178  | -2.0186689 | -1.7461331|
|       | 0.8358662  | -3.3874679 | -2.6977454|
|       | -0.1390907 | -3.7782417 | 3.1955391 |
|       | 0.3689409  | -5.4800658 | 3.2802377 |
|       | 1.5863489  | -4.1879328 | 3.1587410 |
### Optimised structure of $7^+$ radical cation

**Energy** = -1566.683326701

**Coordinates**

| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| C    | -6.4850639 | 0.4399319  | -0.4399644 |
| C    | -6.4104509 | -0.8468070 | 0.1561065  |
| C    | -5.1990378 | -1.4061490 | 0.4509293  |
| C    | -3.9920963 | -0.7083902 | 0.1702870  |
| C    | -4.0680260 | 0.5975292  | -0.4222718 |
| C    | -5.3471657 | 1.1413734  | -0.7234990 |
| C    | -2.7337669 | -1.2575021 | 0.4269953  |
| C    | -1.5515993 | -0.5692387 | 0.1607176  |
| C    | -1.6261478 | 0.7664653  | -0.3779119 |
| C    | -2.8828908 | 1.2899345  | -0.6826186 |
| C    | -0.2802850 | -1.2112239 | 0.3759309  |
| C    | 0.9250610  | -0.4600126 | 0.1294204  |
| C    | 0.8506011  | 0.8759250  | -0.4085771 |
| C    | -0.4207786 | 1.5177043  | -0.6246442 |
| C    | 2.1817204  | -0.9837994 | 0.4339592  |
| C    | 3.3668754  | -0.2908619 | 0.1751124  |
| C    | 3.2910579  | 1.0157061  | -0.4160395 |
| C    | 2.0327837  | 1.5646456  | -0.6734697 |
| C    | 4.6459404  | 0.8346618  | 0.4767306  |
| C    | 5.7838358  | -0.1323443 | 0.1953463  |
| C    | 5.7093243  | 1.1552105  | -0.3969559 |
| C    | 4.4979854  | 1.7143903  | -0.6943962 |
| N    | -0.4259987 | 2.7674529  | -1.1106041 |
| N    | -0.2748914 | -2.4612325 | 0.8615679  |
| C    | -1.1600688 | 3.7908210  | -0.7862602 |
| C    | 0.4565390  | -3.4854274 | 0.5345599  |
| N    | 0.8409994  | -4.4298361 | 1.4409799  |
| C    | 1.3305032  | -5.6181303 | 0.7498963  |
| N    | -1.5463522 | 4.7323294  | -1.6946116 |
| C    | -2.0406808 | 5.9203853  | -1.0066042 |
| C    | 1.7342084  | -5.6429154 | -0.6102935 |
| N    | 0.8769213  | -3.8642359 | -0.7038878 |
| C    | -2.4422221 | 5.3471558  | 0.3551443  |
| N    | -1.5516562 | 4.1710741  | 0.4512566  |
| C    | -1.5163325 | 3.3815979  | 1.6606148  |
| C    | -0.980134  | 4.8257034  | -0.3023861 |
| C    | 0.8141718  | -3.0721870 | -1.9116848 |
| C    | 0.2725411  | -4.5249411 | 2.7692596  |
| H    | -7.4548928 | 0.8620250  | -0.6701424 |
SUPPORTING INFORMATION

|       |       |       |       |
|-------|-------|-------|-------|
| H     | -7.324474 | -1.384574 | 0.372657 |
| H     | -5.141011 | -2.390014 | 0.900510 |
| H     | -5.404738 | 2.122363 | -1.180188 |
| H     | -2.665167 | -2.252575 | 0.845761 |
| H     | -2.959369 | 2.257828 | -1.158726 |
| H     | 2.257905 | -1.952269 | 0.908964 |
| H     | 1.964278 | 2.560048 | -1.091485 |
| H     | 4.703471 | -1.816285 | 0.932050 |
| H     | 6.753599 | -0.554403 | 0.425857 |
| H     | 6.623342 | 1.693734 | -0.613633 |
| H     | 4.439935 | 2.698926 | -1.142519 |
| H     | 2.163964 | -6.069058 | 1.286871 |
| H     | 0.532100 | -6.364454 | 0.651808 |
| H     | -1.245271 | 6.670147 | -0.910654 |
| H     | -2.875932 | 6.366586 | -1.544766 |
| H     | 1.545477 | -5.728026 | -1.436301 |
| H     | 2.791601 | -4.753146 | -0.631392 |
| H     | -3.498775 | 5.054437 | 0.377366 |
| H     | -2.255146 | 6.034741 | 1.179473 |
| H     | -1.437521 | 4.055013 | 2.514326 |
| H     | -2.399939 | 2.747946 | 1.787203 |
| H     | -0.632777 | 2.747866 | 1.642857 |
| H     | -1.716139 | 5.260376 | -3.700303 |
| H     | -0.080070 | 5.451352 | -3.032198 |
| H     | -0.718614 | 3.829721 | -3.372497 |
| H     | 0.733585 | -3.743731 | -2.766728 |
| H     | -0.068044 | -2.436231 | -1.892951 |
| H     | 1.699091 | -2.440494 | -2.036842 |
| H     | -0.634172 | -5.140798 | 2.773663 |
| H     | 1.003742 | -4.971475 | 3.443253 |
| H     | 0.021778 | -3.528323 | 3.123851 |
Optimised structure of 8

Energy = -1566.407692682

Coordinates

C  -4.1568806 -0.4686400 -0.0165610
C  -3.8355473 -1.7398237  0.5077677
C  -2.5256870 -2.1127714  0.6815170
C  -1.4805938 -1.2234915  0.3417760
C  -1.8062001  0.0674611 -0.1808791
C  -3.1647898  0.4173394 -0.3562488
C  -0.1226625 -1.5737305  0.4779200
C   0.8944914 -0.7110493  0.1263223
C   0.5715892  0.6028841 -0.3477441
C  -0.7558354  0.9503325 -0.5029561
C   2.2944340 -1.1515705  0.2178070
C   3.2942279 -0.3681336 -0.5200757
C   2.9882833  0.9781925 -0.9065219
C   1.6556060  1.5457231 -0.6535531
C   4.5272445 -0.8947537 -0.8506997
C   5.5080308 -0.1432108 -1.5287094
C   5.2180033  1.2159768 -1.8666775
C   3.9501323  1.7367916 -1.5404028
C   6.7638280 -0.6882713 -1.8820596
C   7.6953792  0.0836738 -2.5308432
C   7.4121618  1.4280822 -2.8570088
C   6.1987088  1.9839605 -2.5351897
N   1.5273536  2.8266145 -0.7527127
N   2.5384137 -2.2151963  0.9114867
C   0.5139798  3.6428385 -0.4353187
N  -0.1338448  4.3907750 -1.3378743
C  -0.9255495  5.4252929 -0.6570025
C  -0.9878904  4.8935813  0.7824835
N   0.1272368  3.9369662  0.8119391
C   0.4702101  3.2008182  2.0121899
C   0.2317102  4.5189361 -2.7390582
C   3.6907154 -2.7675496  1.3084574
N   4.0868125 -3.9840833  0.9260416
C   5.1803611 -4.4550316  1.7903732
C   5.6530849 -3.1514198  2.4507349
N   4.5036186 -2.2598359  2.2429190
C   4.4934791 -0.8986974  2.7404094
C   3.2945763 -4.9198786  0.1399061
H  -5.1956150 -0.1974111 -0.1527475
H  -4.6325171  -2.4238277  0.7684157
H  -2.2810334  -3.0906322  1.0770291
H  -3.4146953  1.3893198  -0.7640217
H  0.1306392  -2.5583334  0.8479294
H  -1.0234189  1.9130013  -0.9162089
H  4.7589900  -1.9261877  -0.6237493
H  3.7149475  2.7562279  -1.8158956
H  6.9821518  -1.7210223  -1.6387691
H  8.6552584  -0.3372767  -2.8001346
H  8.1597537  2.0191475  -3.3695605
H  5.9806478  3.0129689  -2.7922567
H  -1.9063218  5.5277785  -1.1176934
H  -0.4063493  6.3860157  -0.7201825
H  -1.9260342  4.3704511  0.9911508
H  -0.8482521  5.6712017  1.5314437
H  0.5313136  3.8962279  2.8483320
H  -0.2799400  2.4373220  2.2361795
H  1.4405746  2.7259363  1.8858544
H  0.8457438  5.4095532  -2.8976125
H  0.7872401  3.6397206  -3.0548074
H  -0.6729474  4.6014345  -3.3404588
H  5.9563710  -4.9427411  1.2032957
H  4.7915379  -5.1705261  2.5207371
H  6.5359555  -2.7322342  1.9578457
H  5.8667209  -3.2634948  3.5123124
H  5.1775024  -0.2639080  2.1703915
H  3.4866299  -0.4924165  2.6751125
H  4.7983771  -0.9018880  3.7861111
H  3.9502521  -5.4694890  -0.5345599
H  2.7775674  -5.6308047  0.7899931
H  2.5616387  -4.3727800  -0.4473490
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