A Green Fullerene: Synthesis and Electrochemistry of a Diels–Alder Adduct of [60]Fullerene with a Phthalocyanine

Torsten G. Linssen, Kai Dürr, Michael Hanack* and Andreas Hirsch*

Institut für Organische Chemie, University of Tübingen, Auf der Morgenstelle 18, 72076 Tübingen, Germany

Spectroelectrochemical investigations of a Diels–Alder adduct of [60]fullerene with a nickel phthalocyanine show multiple reductions of both covalently bound electroactive moieties as well as characteristic changes of the optical phthalocyanine properties caused by the reduced fullerene.

One of the characteristic properties of [60]fullerene is its electron deficiency and the ability to undergo multistage reductions with up to six electrons.[1] As a consequence, fulleride salts with outstanding materials properties, for example superconductivity[2] or ferromagnetism,[3] have been synthesised by treating [60]fullerene with electropositive metals or strong organic donor molecules.

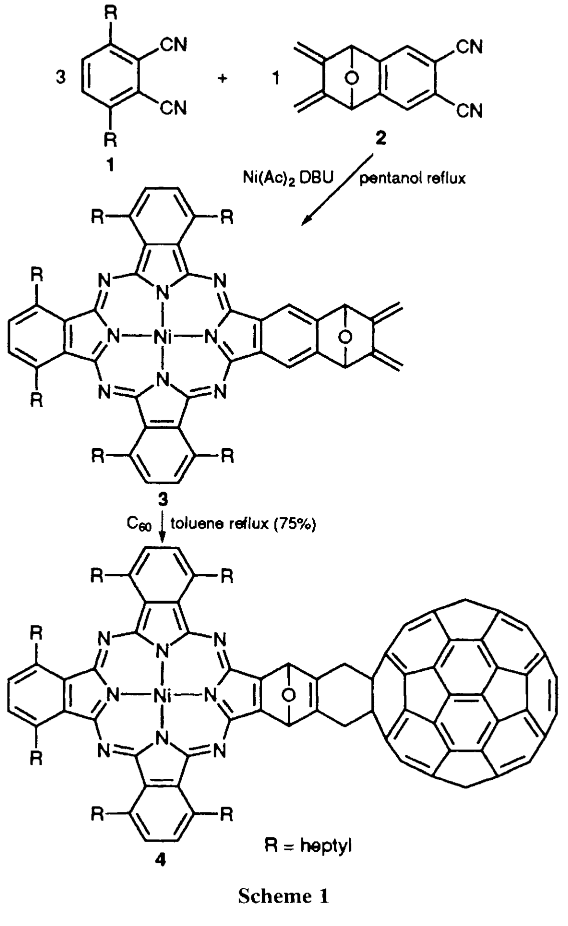
In organic derivatives of [60]fullerene, where the fullerene features are combined with those of other classes of compounds, basic electronic properties of the fullerene core, *e.g.* the ease of electrochemical reductions, are essentially retained.[4] Since [60]fullerene can be modified by a large variety of addition reactions,[5] the opportunity arises to design new molecular devices based on fullerene materials. Here we report the first synthesis and electrochemistry of a Diels–Alder adduct of [60]fullerene with a nickel phthalocyanine. We chose this molecule because phthalocyanines themselves are known for their remarkable electronic and optical behaviour.[6]

Among the suitable ways of chemically modifying the electron deficient polyene [60]fullerene Diels–Alder reactions play an important role.[7] Dienes always add to the 6-6 double bonds of the fullerene core.[5] In this work, the C_s-symmetric nickel phthalocyanine **3** was used as diene. We synthesised this unsymmetrically substituted nickel phthalocyanine for the first time *via* a statistical method[8] by allowing 3 equiv. of 3,6-diheptylphthalodinitrile[9] **1** and 1 equiv. of 1,2,3,4-tetrahydro-2,3-dimethylene-1,4-epoxynaphthalene-6,7-dicarbonitrile[10] **2** to react with nickel acetate in the presence of a catalytic amount of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in pentanol under reflux (Scheme 1). Compound **3** was isolated from other phthalocyanines formed by column chromatography on silica gel using toluene as the mobile phase.

Synthesis of the target compound **4** was accomplished by treating a tenfold excess of [60]fullerene with **3** in refluxing toluene (Scheme 1). After four days all of **3** was consumed (TLC, silica gel, toluene–hexane 1 : 1; R_f = 0.3). The major product **4** was obtained in a 75% yield, smaller amounts of more polar components, presumably higher addition products of [60]fullerene, were also found in the reaction mixture. Isolation of **4** was achieved by column chromatography (silica gel, toluene).

The adduct formation is clearly demonstrated by the comparison of the NMR spectra of **3** and **4**.‡ The resonances (doublet) for the protons at the exocyclic double bonds in **3** at δ 5.4 disappeared whereas in **4** the newly formed methylene protons resonate as multiplets together with the α-methylene protons of the heptyl groups between δ 4.5 and 3.5. In the ^{13}C NMR spectrum of **4**, 47 resonances appear for the sp^2-C atoms with two (δ 143.59 and 143.16) at half intensity as expected for the C_s-symmetry. The UV–VIS spectrum of the green compound **4** shows a split Q-band at 679 and 699 nm which is characteristic for unsymmetrically substituted phthalocyanines[11] (Fig. 1). This phenomenon is due to a decreased degeneracy of the frontier MOs caused by a lowering of symmetry from D_{4h} for symmetrically substituted phthalocyanines to C_s for **4**. The phthalocyanine **3** is also C_s symmetric, but the splitting of the Q-band is too weak to be resolved.[8] This behaviour demonstrates a pronounced influence of the fullerene substituent on the electronic structure of the phthalocyanine ring. In the region between 300 and 500 nm the UV–VIS spectrum of **4** shows superimposed features of **3** with those of a typical [60]fullerene monoaddition product (1,2-adduct). This is especially reflected by the absorption at 436 nm, characteristic for 1,2-adducts of [60]fullerene.[5] The M^+ peak of **4** at 1972 appears as the only signal in the FD MS.

The CV of **4** shows five reversible reductions at −0.41, −0.81, −0.90, −1.26 and −1.53 V *vs.* SCE (Fig. 2). The waves were assigned to the corresponding reduction steps by spectroelectrochemistry (UV–VIS–NIR). The first reduction step is due to the [60]fullerene moiety, which is reflected by the appearance of an absorption at 1074 nm characteristic for a monoanionic [60]fullerene.[12] Interestingly, the reduction of the [60]fullerene moiety has an influence on the electronic structure of the phthalocyanine ring, since the splitting of the Q-band disappeared. This indicates that the splitting of the Q-band decreases with decreasing electron-withdrawing influence of the peripheral substituent. The first reduction of **4** is shifted by about 100 mV compared with [60]fullerene. This is a typical value for a [60]fullerene monoaddition product.[4] The second and third reductions, which are very close to each other, are due to the phthalocyanine and the fullerene moiety, respectively, as demonstrated by the splitting and shift of the Q-band to 582 and



Scheme 1

651 nm, the evolution of a new absorption at 945 nm (phthalocyanine) as well as the disappearance of the 1074 nm band and the development of an absorption at 868 nm (fullerene). The potential for the second reduction at −0.81 V as well as the electronic absorption spectrum is characteristic for singly reduced nickel phthalocyanines.[13] The reduction potential of the second fullerene reduction at −0.90 V is also shifted by about 100 mV to more negative values compared to [60]fullerene.[4] The fourth reduction at −1.26 V is due to the phthalocyanine, reflected by a further shift of the Q-bands to 543 and 650 nm. The reduction potential is typical for the second reduction of a nickel phthalocyanine.[13] Finally, the fifth reduction at −1.53 V is due to the fullerene shown by the disappearance of the 868 nm absorption.

These measurements show that the reduction potentials of both the fullerene and phthalocyanine moieties in **4** do not change significantly compared to separated nickel phthalocyanines or other [60]fullerene monoaddition products. However, the reduction of the fullerene moiety has a pronounced influence on the optical properties of the phthalocyanine. A charge transfer from the phthalocyanine to the fullerene at ambient conditions can be ruled out.

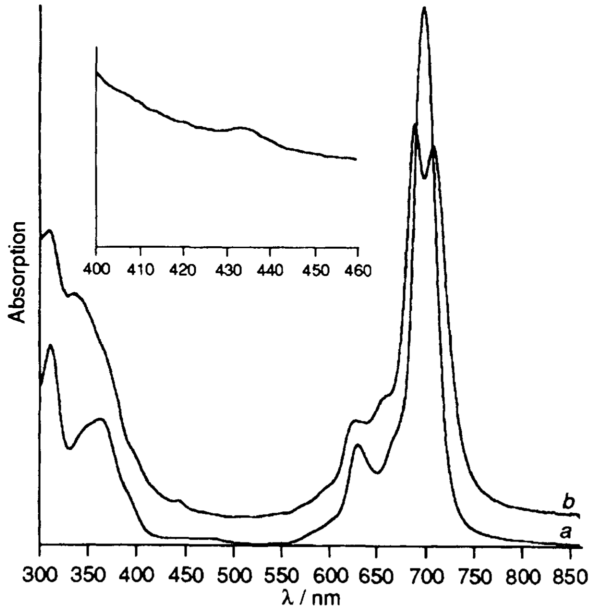


Fig. 1 Electronic absorption spectra (toluene) of **3**(*a*) and **4**(*b*). Inset: the 400–460 nm region for **4**

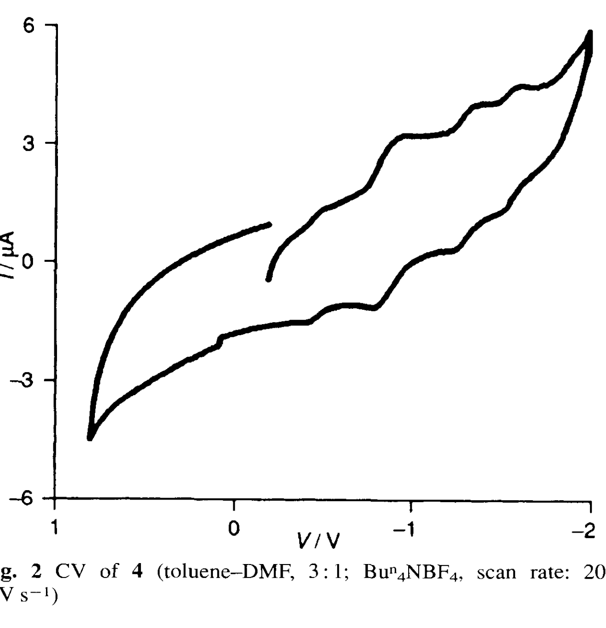


Fig. 2 CV of **4** (toluene–DMF, 3:1; $Bu^n_4NBF_4$, scan rate: 200 mV s^{-1})

We thank the Deutsche Forschungsgemeinschaft (DFG), the Bundesministerium für Forschung und Technologie (BMFT) for financial support and the Hoechst AG for providing us with [60]fullerene.

Received, 15th September 1994; Com. 4/05628K

Footnotes

† Satisfactory spectroscopic and analytical data were obtained for **3**. *Selected spectroscopic data* for **3**: UV–VIS (λ_{max}/nm, toluene) 301, 352, 619, 689; IR ν/cm^{-1} (KBr) 2957, 2924, 2855, 1632, 1609, 1576, 1514, 1466, 1339, 1323, 1265, 1234, 1184, 1094, 887, 760; FD–MS *m/z* 1252.5; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.56 (2H, s, H_{arom}), 7.68 (2H, s, H_{arom}), 7.36 (4H, s, H_{arom}), 6.01 (2H, s, C–H), 5.47 (4H, d, $=CH_2$), 4.16–3.55 (12H, m $-CH_2-$), 2.1–0.7 (78H, m, $-CH_2-$ and –Me).

‡ *Selected spectroscopic data* for **4**: UV–VIS (λ_{max}/nm, toluene) 305, 336, 436, 618, 679, 699; IR ν/cm^{-1} (KBr): 2955, 2924, 2853, 1607, 1516, 1464, 1429, 1325, 1190, 1167, 928, 843, 762, 692, 633, 528; FD–MS *m/z* 1972; ^{1}H NMR (250 MHz, C_6D_6–CS_2) δ 8.85 (2H, s, H_{arom}), 7.81 (2H, s, H_{arom}), 7.61 (4H, m, H_{arom}), 6.44 (2H, s, H_{arom}), 4.5–3.5 (16H, m, $-CH_2-$), 2.1–0.3 (78H, m, $-CH_2-$ and –Me); ^{13}C NMR (62.9 MHz, C_6D_6–CS_2) δ 156.68, 155.39, 154.10, 150.15, 148.09, 147.39, 147.24, 147.07, 146.45, 146.10, 145.82, 145.63, 145.55, 145.50, 145.30, 145.07, 144.85, 144.56, 144.26, 144.16, 143.89, 143.59, 143.43, 143.29, 143.16, 142.37, 142.27, 142.20, 141.97, 141.87, 141.67, 141.47, 141.15, 140.40, 140.16, 139.46, 137.79, 137.74, 137.59, 136.00, 135.39, 135.23, 135.01, 134.46, 131.10, 130.09, 129.54, 66.38, 33.12, 32.65, 31.21, 30.54, 30.43, 30.28, 30.03, 23.67, 23.58, 15.00, 14.78, 1.30.

References

1 Q. Xie, E. Perez-Cordero and L. Echegoyen, *J. Am. Chem. Soc.*, 1992, **114**, 3978.
2 A. F. Hebard, M. J. Rosseinsky, R. C. Haddon, D. W. Murphy, S. H. Glarum, T. T. M. Palstra, A. P. Ramirez and A. R. Kortan, *Nature*, 1991, **350**, 600.
3 P.-M. Allemand, K. C. Khemani, A. Koch, F. Wudl, K. Holczer, S. Donovan, G. Grüner and J. D. Thompson, *Science*, 1991, **253**, 301; P. W. Stephens, D. Cox, J. W. Lauher, L. Mihaly, J. B. Wiley, P.-M. Allemand, A. Hirsch, K. Holczer, Q. Li, J. D. Thompson and F. Wudl, *Nature*, 1992, **355**, 331.
4 M. Maggini, A. Karlson, G. Scorrano, G. Sandonà, G. Farnia and M. Prato, *J. Chem. Soc., Chem. Commun.*, 1994, 589; F. Arias, Q. Xie, Y. Wu, Q. Lu, S. R. Wilson and L. Echegoyen, *J. Am. Chem. Soc.*, 1994, **114**, 6388.
5 For reviews see: R. Taylor and D. R. M. Walton, *Nature*, 1993, **363**, 685; A. Hirsch, *Angew. Chem.*, 1993, **105**, 1189; *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1138; A. Hirsch, *The Chemistry of the Fullerenes*, Thieme, Stuttgart, 1994.
6 H. Schultz, H. Lehmann, M. Rein and M. Hanack, *Struct. Bonding* (Berlin) 1990, **74**, 41.
7 P. Belik, A. Gügel, J. Spikermann and K. Müllen, *Angew. Chem.*,1993, **105**, 95, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 78; A. Gügel, A. Kraus, J. Spikermann, P. Belik and K. Müllen, *Angew. Chem.*, 1994, **106**, 601; *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 559; Y. Rubin, S. Khan, D. I. Freedberg and C. Yeretzian, *J. Am. Chem. Soc.*, 1993, **115**, 344; S. I. Khan, A. M. Oliver, M. N. Paddon-Row and Y. Rubin, *J. Am. Chem. Soc.*, 1993, **115**, 4919; Y.-Z. An, J. L. Anderson and Y. Rubin, *J. Org. Chem.*, 1993, **58**, 4799; B. Kräutler and M. Puchberger, *Helv. Chim. Acta*, 1993, **76**, 1626.
8 For a statistical synthesis of unsymetrically substituted phthalocyanines see also: T. G. Linßen and M. Hanack, *Chem. Ber.*, 1994, **127**, 2051.
9 N. B. McKeown, I. Chambrier and M. J. Cook, *J. Chem. Soc., Perkin Trans. 1*, 1990, 1169.
10 C. Feucht, T. Linßen and M. Hanack, *Chem. Ber.*, 1994, **127**, 113.
11 N. Kobayashi, R. Kondo, S. Nakajima and T. Osa, *J. Am. Chem. Soc.*, 1990, **112**, 9640; H. Konami, Y. Ikeda, M. Hatano and K. Mochizuki, *Mol. Phys.*, 1993, **80**, 153.
12 M. Baumgarten, A. Gügel and L. Gherghel, *Adv. Mater.*, 1993, **5**, 458.
13 A. B. P. Lever, E. R. Milaeva and G. Speier, in *Phthalocyanines: Properties and Application*, ed. C. C. Leznoff and A. B. P. Lever, VCH, New York, 1993, p. 1.