Pergamon

Tetrahedron, Vol. 52, No. 47, pp. 14777-14786, 1996

0040-4020/96 $15.00 + 0.00

PII: S0040-4020(96)00943-X

[4+2]Cycloaddition Reactions of Acenaphth[1,2-a]acenaphthylene

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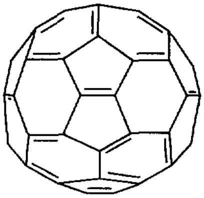
Abstract: Diels-Alder reactions of the annelated pentalene **2** lead to [4.3.3]propellanes. Various substituted anthracenes **3** and cyclopentadienes **5** are tested as diene components. **2** may be classified as a rather electron-rich dienophile. Copyright © 1996 Elsevier Science Ltd

Since the discovery of the fullerenes[1] the chemistry of polycyclic aromatic hydrocarbons has experienced a renaissance. Non-alternant hydrocarbons with annelated five and six-membered rings are a focus of special current research interest.[2] From geometric requirements, fullerenes contain twelve pentagons: according to the "isolated pentagon rule" fused five-membered rings destabilize a fullerene, and indeed, in all fullerenes isolated so far, the pentagons are exclusively surrounded by hexagons.[3]



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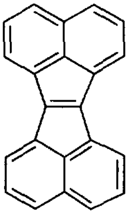

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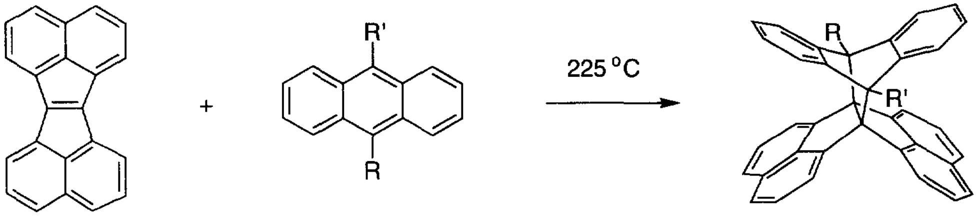
For fullerenes smaller than C_{60} there is only spectroscopic evidence; fullerene C_{50} (**1**, precisely [5,6]-fullerene-C_{50}-D_{5h}), for instance, has been registered by mass spectroscopy[4] and should have five pairs of directly annelated five-membered rings. The hexacyclic pentalene system acenaphth[1,2-a]acenaphthylene (**2**) may be regarded as a non-spherical model compound for fullerene-C_{50} (**1**).

Recently we demonstrated that **2**, with its strained central C-C double bond, reacts as a dienophile in a [4+2]cycloaddition with anthracene (**3.1**).[5] In this paper we report on the reactivity of the pentalene system **2** with various dienes.

Results and Discussion

Among cycloaddition reactions, the Diels-Alder reaction occupies an outstanding position, representing the most important method for the construction of six-membered carbocyclic, and in special cases also heterocyclic rings.[6] Electron-donating and electron-accepting substituents at the diene and the dienophile allow adjustment of the reactivity of the components and lead to functionalized products.



2 **3** **4**

Tab. 1: [4+2]Cycloaddition reactions of **2** with anthracene derivatives **3**; conditions: 3 equiv. of **3**, neat, 225 °C.

diene	R	R'	time [h]	product	yield [%]
3.1	H	H	5	**4.1**	86
3.2	CHO	Cl	2	**4.2**	72
3.3	CN	H	2.5	**4.3**	86
3.4	Cl	Cl	3	**4.4**	89
3.5	Br	Br	3	**4.5**	78
3.6	OCH_3	H	7	**4.6**	78

In general, Diels-Alder reactions of the annelated pentalene **2** should lead to [4.3.3]propellanes. Anthracene derivatives functionalized in the 9,10-positions are of special interest as reactants, because on the one hand they provide an insight into the electronic demand of **2** as a dienophile, and on the other hand they provide a preparative access to substituted propellanes suitable for further transformations.[7]

Homogeneous mixtures of the deep red pentalene system **2** with three equivalents of the anthracene derivatives **3** were heated at 225 °C. The reaction time was determined by controlling via TLC probes until complete conversion. The cycloaddition proceeds significantly faster with the electron-poor dienophiles **3.2**-**3.5**. Nevertheless, with the electron-rich methoxy-substituted anthracene **3.6**, albeit somewhat slower, a good yield is still obtained. According to these results the pentalene **2** should be rated as a rather electron-rich dienophile.

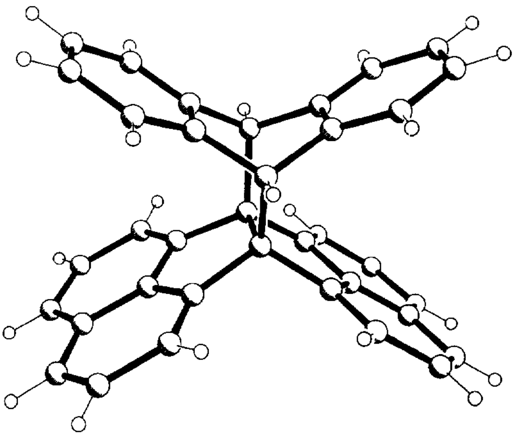
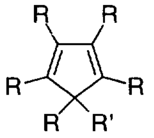


Figure 1. Molecular structure of **4.1**

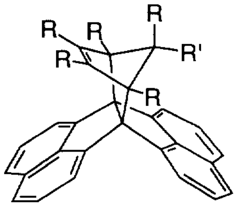
Preliminary experiments with substituted and functionalized cyclopentadienes confirm the electronic preferences observed with the anthracene derivatives **3**. Hexachlorocyclopentadiene (**5.2**), an electron-poor diene, reacts with **2** at 130 °C in solution. In contrast, pentamethylcyclopentadiene (**5.3**) has to be provided neat to achieve a smooth conversion: in the ^{1}H NMR spectrum of the cycloadduct **6.3** the high-field position of the 3H-doublet of a methyl group is evident, presumably caused by the anisotropic effect of the C-C double bond of the cyclohexene moiety. The constitution of this cycloadduct with the exo-oriented methyl group was proved by an X-ray analysis (Figure 2).[8] This methano-bridged [4.3.3]propellane **6.3** exhibits a pronounced elongation of the central single bond C6b-C12b with 162.5, 162.0(6) pm in two independent molecules, indicating a marked ring strain. In comparison, the elongation of the corresponding central propellane bond in the cycloadduct **4.1** of anthracene (**3.1**) is less distinct at 160.5(2) pm (Figure 1).



5.1 R = R' = H

5.2 R = R' = Cl

5.3 R = CH_3, R' = H



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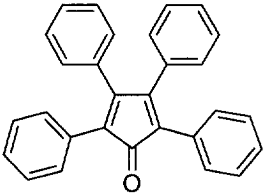

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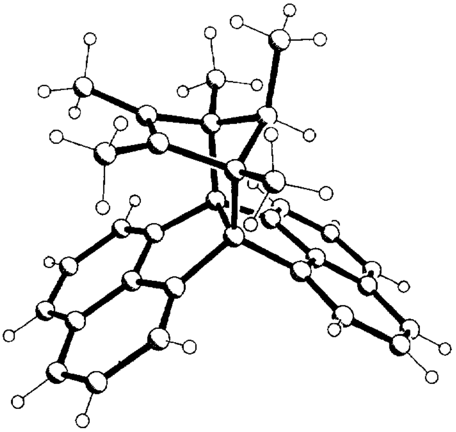
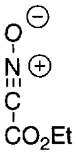


Figure 2. Molecular structure of **6.3**

In the case of the unsubstituted cyclopentadiene (**5.1**) we did not find suitable reaction conditions for a uniform process: according to the mass spectrum a mixture of multiple adducts is formed at the required reaction temperature, for instance a 3:1-adduct with a signal at m/z = 474. Tetraphenylcyclopentadienone (**7**) fails to react with **2**, presumably for steric reasons. A surprise is the inertness of **2** towards 1,3-dipolar cycloaddition: reaction occurs neither with linear dipoles such as the nitrile oxides **8**[9] and **9**[9] and diazomethane, nor with non-linear dipoles such as **10**[10]. The highly electrophilic ozone[11] is the only exception; according to preliminary results, a solution of **2** in dichloromethane is decolorized by ozone in a few seconds at room temperature, giving rise to scarcely soluble oligomeric or polymeric material.



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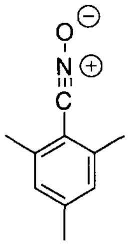

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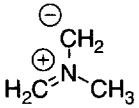

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Obviously the reactivity of the pentalene **2** towards 1,3-dipoles is considerably different from that of fullerene C_{60}, which readily reacts with all of the dipoles[9, 10, 11] discussed here.

Experimental

General: Melting points are uncorrected. - IR: Nicolet 320. - UV/Vis: HP 8452 A. - NMR: Bruker AM 400. ^{1}H-NMR spectra were recorded at 400.1 MHz by using CDCl3 as the solvent and TMS as the internal standard. ^{13}C-NMR spectra were measured at 100.6 MHz by using CDCl3 as the solvent and the internal standard (d = 77.05). - MS: Finnigan MAT 8430. Mass spectra were recorded at an ionizing voltage of 70 eV by electron impact. - For analytical TLC precoated plastic sheets "POLYGRAM SIL G/UV254" from "Macherey-Nagel" were used.

[4+2]Cycloaddition reactions of acenaphth[1,2-a]acenaphthylene (2) with anthracene derivatives 3; general procedure: A mixture of the pentalene system **2** (either 110 mg, 400 µmol or 276 mg, 1.00 mmol) and three equivalents of the anthracene derivative **3** (1.20 mmol or 3.00 mmol) was ground to homogeneity, then allowed to react under nitrogen in a sealed tube (screw-top) for 2-7 h at 220-225 °C (the melting point must be reached; at 200 °C no reaction takes place). Unreacted **3** was removed by sublimation in a Kugelrohr apparatus at 170-220 °C/0.1-0.2 torr. The crude product was purified by flash chromatography and/or recrystallization. Isolated yields of the cycloadducts **4** ranged from 78 to 89 %.

Reaction with anthracene (3.1); 13,18-dihydro-6b,12b[9´,10´]-anthracenoacenaphth[1,2-a]acenaphthylene (4.1): 110 mg (400 µmol) of **2** and 214 mg (1.20 mmol) of **3.1** were allowed to react for 5 h according to the general procedure and unreacted **3.1** was removed by sublimation at 170 °C/0.1 torr. The crude product was recrystallized from dichloromethane/cyclohexane to give 149 mg (86 %) of **4.1** as colorless crystals with mp 322 °C (for selected spectroscopic data: ref.[5]). Crystal data[8] for compound **4.1**: $C_{36}H_{22}$, monoclinic, space group $P2_1/n$, a = 1024.5(4), b = 1444.8(5), c = 1612.8(6) pm, β = 101.56(3)°, V = 2.339 nm^3, Z = 4, D_x = 1.291 Mg m^{-3}, λ(Mo $K\alpha$) = 71.073 pm, μ = 0.07 mm^{-1}, T = -95 °C. *Data collection and reduction*: A colorless prism ca. 0.5 x 0.45 x 0.45 mm was mounted in inert oil. Data were collected to $2\theta_{max}$ 50° on a Stoe STADI-4 diffractometer fitted with a Siemens LT-2 low temperature attachment. Of 6071 data, 4132 were unique. *Structure solution and refinement*: The structure was solved by direct methods and refined anisotropically on F^2 using all reflections (program SHELXL-93, G. M. Sheldrick, University of Göttingen). Hydrogen atoms were included by using a riding model. The final $wR(F^2)$ was 0.113 for 326 parameters, conventional $R(F)$ 0.041. S = 1.02; max. Δ/σ <0.001; max. $\Delta\rho$ 212 e nm^{-3}.

Reaction with 10-chloroanthraldehyde (3.2); 18-chloro-13,18-dihydro-6b,12b[9´,10´]anthracenoacenaphth[1,2-a]acenaphthylene-13-carboxaldehyde (4.2): 110 mg (400 µmol) of **2** and 289 mg (1.20 mmol) of **3.2** were allowed to react for 2 h according to the general procedure and unreacted **3.2** was removed by sublimation at 200 °C/0.15 torr. The crude product was washed four times with 1 ml trichloromethane and once with 1 ml dichloromethane to give 149 mg (72 %) of **4.2** as colorless crystals with mp 264-265 °C (dec.). - IR (KBr): ν = 3065 cm^{-1} (w), 2820 (w), 2723 (w), 1741 (s), 1589 (m), 1457 (m), 1364 (w), 944 (w), 809 (m), 784 (s), 758 (s), 719 (ml, 571 (m), 546 (w). - UV (acetonitrile): λ_{max} (lg ε) = 214 nm (4.96), 228 (sh, 4.67), 268 (sh, 3.73), 286 (4.09), 308 (4.06), 320 (sh, 4.03). - ^1H NMR: δ = 6.85 (m, 2H), 6.92 (m, 2H), 7 00 (m, 2H), 7.34-7.41 (m, 8H), 7.60 (m, 2H), 8.10 (m, 4H), 10.96 (s, 1H, CHO). - ^{13}C NMR: δ = 64.39 (s), 121.27 (d), 122.60 (d), 123.05 (d), 123.99 (d), 124.19 (d), 124.55 (d), 126.74 (d), 127.43 (d), 127.87 (d), 131.26 (s), 136.38 (s), 139.55 (s), 139.89 (s), 142.96 (s), 143.47 (s), 200.78 (d, C=O); some signals could not be detected (one "d" and three "s"), because of the low solubility of the compound and the low intensity of the signals. - MS: m/z (%): 516/518 (0.2/0.05) [M$^+$], 276 (100), 176 (4), 138 (7). - $C_{37}H_{21}ClO$ (517.0): calcd. C 85.85, H 4.09; found C 85.94, H 3.90.

Reaction with 9-cyanoanthracene (3.3); 13-cyano-13,18-dihydro-6b,12b[9′,10′]anthracenoacenaphth[1,2-a]acenaphthylene (4.3): 110 mg (400 µmol) of **2** and 244 mg (1.20 mmol) of **3.3** were allowed to react for 2.5 h according to the general procedure and unreacted **3.3** was removed by sublimation at 170 °C/0.2 torr. The crude product was washed four times with 1 ml trichloromethane and once with 1 ml dichloromethane to give 165 mg (86 %) of **4.3** as colorless crystals with mp 266-268 °C (dec., Retro-Diels-Alder reaction). - IR (KBr): ν = 3030 cm^{-1} (m), 1621 (w), 1600 (m), 1492 (w), 1462 (w), 1359 (w), 815 (w), 778 (s), 761 (m). - UV (acetonitrile): λ_{max} (lg ε) = 212 nm (4.78), 268 (sh, 3.58), 276 (sh, 3.73), 286 (3.86), 304 (3.95), 320 (3.89). - ^{1}H NMR: δ = 5.16 (s, 1H, 18-H), 6.81 (m, 4H), 7.02 (m, 2H), 7.34 (m, 2H), 7.39-7.47 (m, 8H), 7.69 (m, 2H), 8.17 (m, 2H). - ^{13}C NMR: δ = 54.78 (d, C-18), 55.50 (s), 74.26 (s), 74.36 (s), 75.13 (s), 118.33 (d), 118.55 (s), 119.88 (d), 123.74 (d), 123.84 (d), 124.41 (d), 125.49 (d), 126.14 (d), 127.02 (d), 127.95 (d), 128.24 (d), 131.38 (s), 136.05 (s), 139.05 (s), 143.19 (s), 145.10 (s). - MS: m/z (%): 479 (0.6) [M$^+$], 276 (100), 203 (7), 138 (8). - $C_{37}H_{21}N$ (479.6).

Reaction with 9,10-dichloroanthracene (3.4); 13,18-dihydro-13,18-dichloro-6b,12b[9′,10′]anthracenoacenaphth[1,2-a]acenaphthylene (4.4): 110 mg (400 µmol) of **2** and 296 mg (1.20 mmol) of **3.4** were allowed to react for 3 h according to the general procedure and unreacted **3.4** was removed by sublimation at 210 °C/0.2 torr. The crude product was washed twice with 1 ml dichloromethane to give 185 mg (89 %) of **4.4** as colorless needles with mp 338-340 °C (dec.). - IR (KBr): ν = 3059 cm^{-1} (w), 1592 (w), 1452 (m), 1365 (w), 1176 (m), 1039 (w), 957 (m), 816 (w), 785 (s), 758 (s), 736 (w), 712 (m), 652 (w), 591 (w), 546 (w). - UV (acetonitrile): λ_{max} (lg ε) = 212 nm (4.98), 252 (sh, 3.67), 274 (3.93), 286 (4.09), 306 (4.08). - ^{1}H NMR: δ = 6.90 (m, 4H), 7.36-7.44 (m, 8H), 7.51 (m, 4H), 8.11 (m, 4H). - ^{13}C NMR: δ = 78.49 (s), 80.35 (s), 121.35 (d), 123.39 (d), 124.26 (d), 126.90 (d), 127.47 (d), 131.14 (s), 138.63 (s), 139.54 (s), 142.98 (s). - MS: m/z (%):522/524 (0.2/0.2) [M$^+$], 452 (0.8), 276 (100), 246 (3), 138 (5). - $C_{36}H_{20}Cl_2$ (523.5): calcd. C 82.60, H 3.85; found C 82.56, H 3.85.

Reaction with 9,10-dibromoanthracene (3.5); 13,18-dihydro-13,18-dibromo-6b,12b[9´,10´]anthracenoacenaphth[1,2-a]acenaphthylene (4.5): 276 mg (1.00 mmol) of **2** and 1.01 g (1.20 mmol) of **3.5** were allowed to react for 3 h according to the general procedure and unreacted **3.5** was removed by sublimation at 220 °C/0.1 torr. The crude product was purified by flash chromatography (silica/toluene) and by recrystallization from trichloromethane to give 477 mg (78 %) of **4.5** as colorless crystals with mp 328-329 °C (dec.). - IR (KBr): ν = 3060 cm^{-1} (w), 2925 (w), 1592 (m), 1553 (m), 1366 (w), 1168 (m), 937 (m), 784 (s), 758 (s), 722 (m), 704 (m), 546 (w). - UV (acetonitrile): λ_{max} (lg ε) = 214 nm (4.98), 266 (sh, 3.85), 276 (4.03), 286 (4.16), 308 (4.09). - ^{1}H NMR: δ = 6.89 (m, 4H), 7.35-7.44 (m, 8H), 7.60 (m, 4H), 8.22 ("d", "J" = 6.9 Hz, 4H). - ^{13}C NMR: δ = 77.63 (s), 81.52 (s), 121.57 (d), 124.35 (d), 126.10 (d), 127.24 (d), 127.25 (d), 131.11 (s), 138.84 (s), 139.51 (s), 143.17 (s). - MS: m/z (%): 610/612/614 (0.3/0.6/0.3) [M^{+}], 530/532 (0.3/0.3), 452 (3), 334/336/338 (2/4/2), 277 (26), 276 (100), 176 (5). - $C_{36}H_{20}Br_{2}$ (612.4): calcd. C 70.61, H 3.29; found C 70.66, H 3.16.

Reaction with 9-methoxyanthracene (3.6); 13-methoxy-13,18-dihydro-6b,12b[9´,10´]anthracenoacenaphth[1,2-a]acenaphthylene (4.6): 110 mg (400 µmol) of **2** and 250 mg (1.20 mmol) of **3.6** were allowed to react for 7 h according to the general procedure and unreacted **3.6** was removed by sublimation at 220 °C/0.2 torr. The crude product was washed four times with 1 ml dichloromethane to give 152 mg (78 %) of **4.6** as colorless crystals with mp 276-277 °C (dec.). - IR (KBr): ν = 3066 cm^{-1} (w), 3040 (m), 3017 (w), 2935 (w), 1594 (w), 1496 (w), 1457 (m), 1240 (m), 1218 (m), 1134 (m), 1080 (s), 788 (s), 772 (m), 757 (s), 735 (m), 589 (m), 549 (w). - UV (acetonitrile): λ_{max} (lg ε) = 212 nm (4.97), 276 (3.94), 288 (4.07), 306 (4.08), 316 (4.06). - ^{1}H NMR: δ = 4.16 (s, 3H, OCH3), 5.03 (s, 1H), 6.72 (m, 4H), 6.99 (m, 2H), 7.16 (m, 2H), 7.31-7.40 (m, 8H), 7.58 (m, 2H), 7.98 (m, 2H). - ^{13}C NMR: δ = 55.15 (d), 56.98 (q, C-23), 89.78 (s), 117.88 (d), 121.38 (d), 123.13 (d), 123.34 (d), 123.80 (d), 124.85 (d), 125.09 (d), 125.53 (d),127.40 (d), 127.85 (d), 131.19 (s), 139.30 (s), 139.53 (s), 140.13 (s), 144.81 (s), 146.02 (s); two singuletts could not be detected, because of the low solubility of the compound and the low intensity of the signals. - MS: m/z (%): 484 (0.4) [M^{+}], 276 (100), 217 (25), 193 (14), 138 (4). - $C_{37}H_{24}O$ (484.6): calcd. C 91.71, H 4.99; found C 91.64, H 4.84.

Reaction with pentamethylcyclopentadiene (5.3): A mixture of 110 mg (400 µmol) of **2** and 272 mg (2.00 mmol) of **5.3** was stirred for 30 min at 130 °C. TLC (silica, hexanes): R_f = 0.51, 0.30, 0 16, 0.13, 0.10 (**6.3**), 0.00. The fraction with R_f = 0.10 is isolated by flash chromatography: 120 mg (73 %) of 11-exo-7,8,9,10,11-pentamethyl-7,10-methano-6b,7,10,10a-tetrahydro-6b,10a[1′,8′]naphthalenofluoranthene (**6.3**) as colorless crystals with mp 239-240 °C (dec.). - IR (KBr): ν = 3039 cm^{-1} (m), 2954 (m), 2927 (m), 2912 (m), 2869 (m), 2851 (m), 1619 (w), 1593 (m), 1495 (m), 1450 (m), 1444 (w), 1417 (w), 1374 (m), 1361 (m), 1148 (w), 1089 (w), 1019(w), 808 (w), 782 (s), 778 (s). - UV (acetonitrile): λ_{max} (lg ε) = 218 nm (4.96), 278 (sh, 3.84), 288 (3,98), 306 (4.07), 314 (sh, 4.05). ^1H NMR: δ = 0.51 (d, J = 6.4 Hz, 3H, $CHC\underline{H}_3$), 0.96 (s, 6H), 1.54 (s, 6H), 1.74 (q, J = 6.4 Hz, $C\underline{H}CH_3$), 7.35 (m, 2H), 7.45-7.50 (m, 4H), 7.59 (m, 4H), 7.64 ("d", "J" = 6.9 Hz, 2H). - ^{13}C NMR: δ = 8.45 (q), 11.42 (q), 12.47 (q), 58.50 (d, C-17), 59.17 (s, C-13/C-16), 79.41 (s, C-6b/C-12b), 118.87 (d), 120.88 (d), 123.14 (d), 123.42 (d), 127.21 (d), 127.61 (d), 131.63 (s), 135.35 (s), 140.55 (s), 141.53 (s), 145.36 (s), 146.78 (s); one "s" is superimposed. - MS: m/z (%): 413 (0.3), 412 (0.5) [M^+], 276 (100), 136 (6), 121 (5). - $C_{32}H_{28}$ (412.6): calcd. C 93.16, H 6.84; found C 93.13, H 6.84. Crystal data[8] for compound **6.3**: $C_{32}H_{28}$, monoclinic, space group $P2_1/c$, a = 1939.4(5), b = 1436.5(4), c = 1719.4(5) pm, β = 111.42(3)°, V = 4.459 nm^3, Z = 8, D_x = 1.229 Mg m^{-3}, μ = 0.07 mm^{-1}, T = -100 °C. *Data collection and reduction*: Colorless prism 0.8 x 0.38 x 0.12 mm, 9151 data, 7871 unique. *Structure solution and refinement*: $wR(F^2)$ 0.228 for 587 parameters, $R(F)$ 0.061, S = 1.00, max. $\Delta\rho$ 241 e nm^{-3}. All other details as above. The two independent molecules are closely similar, with a mean deviation of 5 pm for a least-squares fit of all non-H atoms.

Acknowledgement: Financial support of the "Deutsche Forschungsgemeinschaft" and of the "Fonds der Chemischen Industrie" is gratefully acknowledged.

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8. Further details of the crystal structure investigations are available on request from Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldhafen, on quoting the depository number CSD-405626 for compound **4.1** and CSD-405627 for compound **6.3**, the names of the authors, and the journal citation.
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(*Received in Germany* 13 *August* 1996; *accepted* 7 *October* 1996)