12 s. Acetone ($\delta = 225$, CO) undergoes aldol condensation to 4-hydroxy-4-methylpentan-2-one (observed by gas chromatography (GC) in the product stream), which is dehydrated to 4-methylpent-3-en-2-one on the zeolite. Cracking of acetone dimers produces acetic acid ($\delta = 180$, COOH) and isobutylene (observed by GC). Oligomerization, isomerization, and cracking of hydrocarbons formed from isobutene result in many products that show other signals in the ^{13}C NMR spectra (Figure 2) and the gas chromatogram. Comparison of the spectra in Figure 2 with those from conventional in situ studies of this reaction suggests that there is no loss of acetone or other volatile species during transfer from the reactor to the MAS-NMR rotor.

Figure 2 also shows the development of strong ^{13}C NMR signals at $\delta = 249$, 145 (partially overlapped), and 47 after 2 to 12 s. This unique cluster of chemical shifts is the signature of alkyl-substituted cyclopentenylcarbenium ions; the 1,3-dimethylcylopentenyl cation shown in Figure 2 is a simple example of such a species. This very stable class of carbenium ion was previously observed in an early in situ NMR study of propene oligomerization,[12] but not in conventional in situ studies of acetone chemistry.

We have demonstrated a powerful experimental tool for studying reaction mechanisms of heterogeneous catalysis. The pulse–quench reactor can be used to prepare samples for NMR study under conditions identical to those for microreactor studies. In particular, in situ NMR spectrscopy can now be applied to probe reactions at appreciably higher temperatures and with continuous removal of volatile products from the catalyst. For the first time, NMR studies of irreversible reactions on zeolites have been carried out on time scales shorter than typical catalyst contact times.

Experimental Section

The catalyst was prepared from zeolite powder (Si/Al = 19) mixed with a minimum amount of alumina binder (typically 30 wt%) and extruded into pellets with a diameter of 1 mm. The catalyst (0.25 g, dry weight) was packed into a stainless steel tube (inner diameter 7.5 mm, outer diameter 10 mm) to form a bed that is 8 mm long. The entire length of the tube (5.5 cm) was heated to a controlled temperature with heating tape, and the catalyst was activated in the pulse–quench reactor under a flow of He immediately prior to reaction. The catalyst bed was isolated immediately following the quench and transferred to a MAS rotor, which was sealed in a glovebox at room temperature. The sample was at no time exposed to the atmosphere. Solid-state ^{13}C MAS NMR spectra were measured at 75.4 MHz with cross polarization on a Chemagnetics CMX-300 spectrometer.

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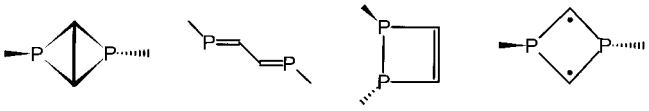
Valence Isomerization in the Solid State: From 1,3-Diphosphacyclobutane-2,4-diyl to 1,2-Dihydro-1,2-diphosphete**

Olaf Schmidt, André Fuchs, Dietrich Gudat, Martin Nieger, Wilfried Hoffbauer, Edgar Niecke,* and Wolfgang W. Schoeller*

Dedicated to Professor Achim Müller on the occasion of his 60th birthday

Four-membered heterocycles of the type $P_2C_2R_4$ have attracted a great deal of interest as building blocks in organophosphorus and organometallic chemistry.[1] Within the series 2,4-diphosphabicyclobutane (**I**), 1,4-diphosphabutadiene (**II**), and 1,2-dihydro-1,2-diphosphete (**III**), the bicyclic system is the least and the 1,2-diphosphete the most stable valence isomer.[2] Hence, it appears logical that the most important synthetic route to **III** involves the valence isomerization of 1,4-diphosphabutadienes.[3]



I **II** **III** **IV**

Recently we proved the existence of another valence isomer of **I**–**III**, the biradicaloid 1,3-diphosphacyclobutane-2,4-diyl (**IV**).[4] Although compounds of type **IV** are even less stable than those of type **I**, isolable derivatives do exist owing to the fact that isomerization to **I** by formation of a transannular C–C bond is forbidden according to the Woodward–Hoffmann rules. To gain more insight into the chemistry of

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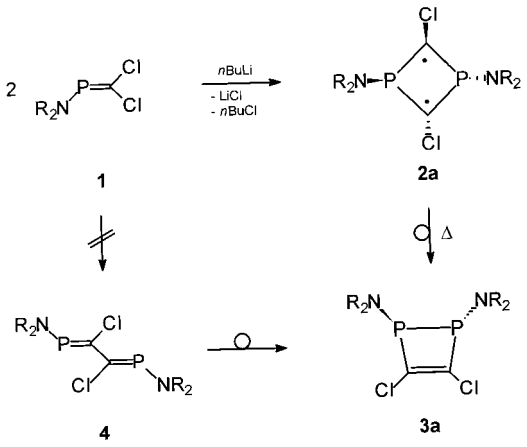
such biradicaloid compounds, we investigated the effect of introducing amino substituents at the phosphorus positions. This was expected to increase the barrier to inversion at phosphorus and inhibit the delocalization of electron density in the P_2C_2 cycle, and thus bring the biradical character to the fore. Here we report on the synthesis of a 1,3-diamino-1,3-diphosphacyclobutane-2,4-diyl and its valence isomerization to a 1,2-dihydro-1,2-diphosphete in the solid state, as well as a likely mechanism involving an intermediate phosphanylcarbene.

Treatment of the amino(dichloromethylene)phosphane $R_2NP{=}CCl_2$ (**1**, $R_2 = 2,2,6,6\text{-}Me_4C_5H_6N$)[5] with *t*BuLi (0.5 equiv) under conditions similar to those employed for the synthesis of $[(2,4,6\text{-}t\text{Bu}_3C_6H_2)PC(Cl)]_2$ (**2b**)[4] ($-110\,^\circ$C, THF, stirring at $-80\,^\circ$C for 4 h) resulted in the precipitation of a deep purple solid, which was isolated in 70% yield after filtration at $-80\,^\circ$C (Scheme 1).[6] Recrystallization of the



Scheme 1. Synthesis of **3a**.

crude product from toluene at $-30\,^\circ$C afforded colorless crystals, whose solution MS (*m*/*z*: 436, $C_{20}H_{36}Cl_2N_2P_2$) and ^{31}P NMR data ($\delta = 17.4$ (s)) are in agreement with the expected constitution of 1,3-diamino-1,3-diphosphacyclobutane-2,4-diyl **2a**. However, according to the ^{13}C NMR spectra, the ring carbon atom is strongly deshielded with respect to that of **2b** (δ(**2a**) = 129.3, δ(**2b**) = 98.8[4]), and the deviations from an ideal 1:2:1 triplet pattern suggest the presence of an AA′X ($\Sigma J_{CP} = 13.4$ Hz) rather than an A_2X spin system.[7] A spectrum of this type is in agreement with the presence of 1,2-dihydro-1,2-diphosphete[21] **3a** rather than biradicaloid **2a**.

This constitution was confirmed by an X-ray crystal structure determination,[8] which revealed the presence of a folded four-membered P_2C_2 ring. The phosphorus atoms are located in the 1,2-positions, and there is a slightly twisted C–C double bond, as indicated by the P1-C1-C2-P2 dihedral angle of $-24.4(3)^\circ$ (Figure 1). The degree of pyramidalization at the phosphorus atoms (the sums of valence angles at P1 and P2 are 302 and 303°, respectively) is typical for saturated phosphorus(III) centers, and the *trans* orientation of the bulky amino substituents minimizes steric hindrance. Quite

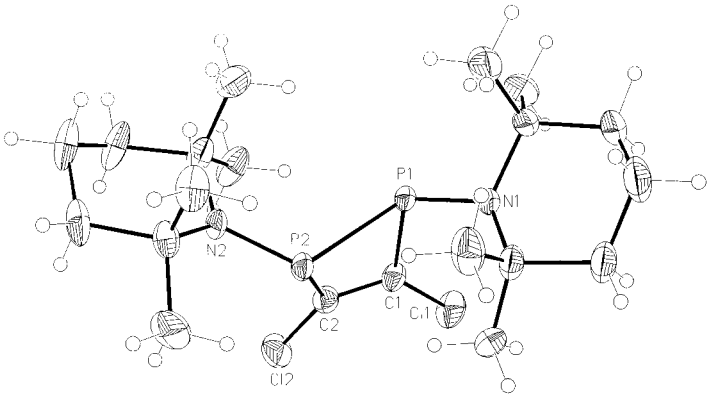


Figure 1. Molecular structure of **3a**; hydrogen atoms have been omitted for clarity. Important bond lengths [pm], bond angles [°], and torsion angles [°]: P1–P2 232.5(1), P1–C1 179.7(4), P2–C2 180.7(4), C1–C2 134.4(5), P1–N1 169.6(3), P2–N2 168.8(3), C1–Cl1 171.9(3), C2–Cl2 171.0(4); P2-P1-C1 73.1(1), P1-P2-C2 73.1(1), P1-C1-C2 104.2(2), C1-C2-P2 103.4(3), P2-P1-N1 118.0(1), C1-P1-N1 111.2(2), P1-P2-N2 118.7(1), C2-P2-N2 111.3(2), P1-C1-Cl1 128.6(2), C2-C1-Cl1 127.1(3), P2-C2-Cl2 128.9(2), C1-C2-Cl2 127.5(3); P1-C1-C2-P2 −24.4(3), Cl1-C1-C2-Cl2 −15.1(5), C1-P1-P2-C2 −14.3(2), N1-P1-P2-N2 134.9(2), P2-P1-C1-C2 19.1(2), P1-P2-C2-C1 18.9(2)

remarkably,the P1–P2 bond (232.5(1) pm) is substantially larger than known P–P single bonds in 1,2-dihydro-1,2-diphosphetes (219[10] to 225 pm[11]). The remaining bond distances and angles reveal no peculiarities.

Knowing that 1,2-dihydro-1,2-diphosphetes may arise from electrocyclic ring closure of 1,4-diphosphabutadienes,[12] we undertook a closer investigation of the initially formed purple precipitate to probe the occurrence of diene **4** (which might result from reductive coupling[13] of two molecules of **1**) as a possible intermediate. While analysis by X-ray powder diffraction gave no observable reflections, which is indicative of a very low degree of crystallinity of the sample, solid-state UV/Vis and CP/MAS NMR studies revealed that the precipitate is not composed of **3a**, but rather a new species, which must therefore be considered as an isolable intermediate of the overall reaction. However, even if a high-resolution mass spectrum (*m*/*z*: 436.732, calcd for $C_{20}H_{36}Cl_2N_2P_2$: 435.731) shows the product to be an isomer of **3a**, the appearance of a characteristic UV/Vis absorption band ($\lambda_{max} = 567$ nm, cf. $\lambda_{max} = 356$ nm for **2b**[4]) and the similarity of the isotropic ^{31}P and ^{13}C chemical shifts of the ring atoms ($\delta_{iso} = 18.9$ (^{31}P), 99.0 (^{13}C)) with those of **2b**[4] ($\delta_{iso} = 26.1$ (^{31}P), 100(^{13}C)) suggest a formulation as biradicaloid **2a** rather than a 1,4-diphosphadiene.

This assignment is further supported by the fact that the spinning sidebands in the solid-state ^{31}P MAS NMR spectra of **2a** (Figure 2) and **2b**[4] appear as singlets. This suggests a parallel alignment of all three principal axes of the two shielding tensors and implies that both tensors are related by a center of symmetry.[13] This condition can be fulfilled by biradicaloids of type **IV**, which, according to crystallographic and theoretical investigations,[4] possess molecular C_i symmetry, but not by a diphosphete of the type **II**, which may exhibit either C_2 or C_s symmetry (crystalline **3a** approximately displays noncrystallographic C_2 symmetry). Consequently, and in contrast to the case of **2a**, the spinning sidebands in the

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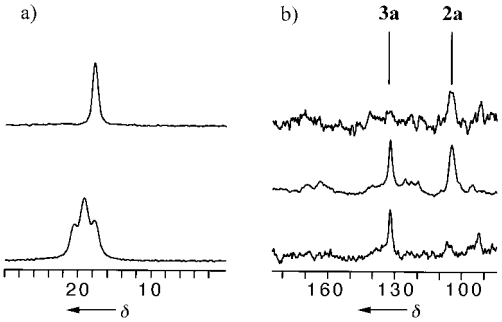
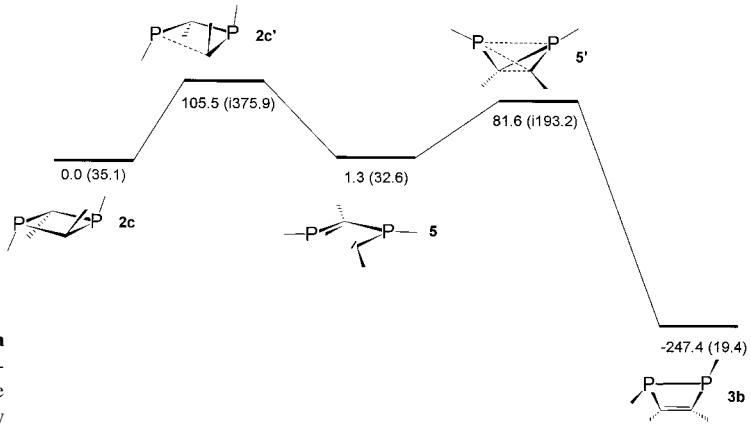


Figure 2. a) Section (centerband) of the ^{31}P MAS NMR spectra of solid **2a** (161.9 MHz, 40 transients, MAS frequency 7.044 kHz, top) and **3a** (recrystallized sample, 40 transients, MAS frequency 10.07 kHz, bottom). b) The olefinic region of the ^{13}C CP/MAS spectrum (100 MHz) of a freshly prepared sample of **2a** at ambient temperature. Top: 60 transients recorded immediately after sample preparation (measurement time 12 min); middle: 4000 transients (total measurement time 13.33 h); bottom: 80 transients (measurement time 16 min) immediately after the long-time acquisition. Signals without labels represent spinning sidebands of the resonances (not shown) of the tetramethylpiperidinyl substituents. The change in intensities of the labeled signals indicates the almost complete conversion **2a** → **3a** within the duration of the experiment.



Scheme 2. Schematic representation of the calculated stationary points and transition states on the electronic hypersurface for the reaction of **2c** to **3b** at the MCSCF(10,10) level. The relative energies are given in kJ mol^{-1}, and the values in parentheses indicate the lowest vibrational frequencies. The structures **2c′** and **5′** represent transition states and exhibit one imaginary vibrational frequency.

^{31}P MAS spectrum of **3a** consist of multiplets (Figure 2a) whose splittings vary with changing rotational speed. The ^{31}P spin pairs can thus be classified as an AB spin system, and the observed splitting represents a superposition of scalar and residual dipolar coupling contributions.[14]

Further investigations revealed that the conversion **2a** → **3a** is not only promoted by treatment of solid **2a** with a variety of solvents, but occurs also in the solid state. The isomerization can be monitored by the decay of the long-wave UV/Vis absorption band of **2a** as well as by ^{31}P and ^{13}C CP/MAS NMR spectroscopy (Figure 2b). Compared to the case in solution, where complete conversion of **3a** is achieved spontaneously, the rearrangement proceeds at a lower rate and takes days to complete at ambient temperature. The samples isomerize faster upon gentle heating or storing under MAS conditions for a prolonged period (more than 90% conversion in less than 20 h, Figure 2b).

The structural findings for **3a** are in accordance with the results of ab initio calculations at the MP2/6-31g(d,p) level on the model compound *cyclo*-[-(H$_2$N)P–C(Cl)=C(Cl)–P-(NH$_2$)-],[15] which gave the following bond lengths: P–P 230.9, C–P 180.8, C=C 136.2 pm. The lengthening of the P–P bond with respect to the parent compound *cyclo*-[-(H)P–C(H)=C(H)–P(H)-] (**3b**, P–P 222 pm) results, according to a population analysis, from a slightly higher p character in the bond and is accompanied by a shortening of the adjacent P–C bonds.

To gain further insight into the solid-state valence isomerization of **2a** to **3a**, we performed ab initio calculations on the parent compounds **2c** and **3b**, and further characterized the transition between these states on the electronic hypersurface. All calculations were performed at the MCSCF(10,10)/6-31g(d) level to ensure a proper treatment of the biradical and other open-shell structures.[16] According to the results, the isomerization of **2c** (^1A_g, C_i symmetry) to **3b** is a two-step process through an additional stationary point on the hypersurface, which was identified as the singlet phosphanylcarbene **5** (Scheme 2).[17] The rate-determining step ($\Delta E =$ 105.5 kJ mol^{-1}) is the ring opening of biradicaloid **2c** to give **5**, which is only 1.3 kJ mol^{-1} higher in energy than **2c**. The transition state for this reaction step (**2c′**, Scheme 2) is reached from **2c** by partial rupture of one P–C bond (244.2 pm) and a conrotatory twist of the hydrogen atoms at C(P). In **5** this P–C bond is completely broken (355.7 pm), and the other parameters (e.g. P–C bond distances 164.3, 181.3, 171.6 pm) indicate the formation of a planar, butadiene-like structure. Further conrotatory movement of the hydrogen atoms at P(C) leads to a second transition state **5′** (C_1 symmetry, ^{1}A) with a tetrahedrane-like structure in which the new P–P (321.6 pm) and C–C (245.8 pm) bonds are already partially formed. The final product, the 1,2-dihydro-1,2-diphosphete **3b**,[4] marks the lowest point on the electronic hypersurface (–247.0 kJ mol^{-1} with respect to **2c**).

The MCSCF calculations suggest a novel reaction pathway for the 1,3-diphosphacyclobutane-2,4-diyl ⇌ 1,2-dihydro-1,2-diphosphete rearrangement, which proceeds via an intermediate phosphanylcarbene[18] and requires only relatively small changes in the ring bonds throughout the entire reaction. Investigations of further aspects of the thermally induced rearrangement in solution,[20] as well as of the corresponding photochemically induced reaction, are in progress.

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Keywords: ab initio calculations · diradicals · NMR spectroscopy · phosphorus heterocycles · valence isomerization

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[6] **2a**: A solution of *t*BuLi (4.7 mmol, 2.8 mL of a 1.7 M solution in hexane) was added dropwise to a solution of **1** (2.4 g, 9.4 mmol) in

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THF (100 mL) at −105 °C. The reaction mixture was slowly warmed to −80 °C and stirred for 4 h. The resulting purple solid was separated by filtration at −80 °C to afford **2a** (1.44 g, 70 %). **3a**: A solution of *t*BuLi (4.7 mmol, 2.8 mL of a 1.7 M solution in hexane) was added dropwise to a solution of **1** (2.4 g, 9.4 mmol) in THF (100 mL) at −105 °C. The reaction mixture was slowly warmed to room temperature under stirring, and the solvents were removed in vacuo. The residue was washed with *n*-pentane (50 mL), and precipitated LiCl was separated by filtration. Removal of the solvent in vacuo afforded **3a** as beige crystals (1.93 g, 93 %; m.p. 148–149 °C).

[7] **3a**: ^{31}P NMR (121 MHz, THF, 303 K): $\delta = 18.9$; ^{1}H NMR (300 MHz, C_6D_6): $\delta = 1.5$ (m, 36H; CH_2, CH_3); ^{13}C NMR (75.47 MHz, C_6D_6, 303 K): $\delta = 129.3$ (pseudo t, $\Sigma J = 13.4$ Hz; *C*=*C*), 58.9 (s; *C*NP), 42.1 (s; *C*CN), 31.6 (pseudo t, $\Sigma J = 6.3$ Hz; C_2CNP), 17.7 (s, *C*CCN); UV/Vis (1 % $BaSO_4$ solution): $\lambda_{max} = 567$ nm; MS (40 eV, EI): *m*/*z* (%): 436 (22) [M^+], 421 (20) [$M^+ - CH_3$], 401 (4) [$M^+ - Cl$], 296 (13) [$M^+ - C_9H_{18}N$), 230 (20) [$C_{11}H_{18}ClNP^+$], 126 (37) [$C_9H_{18}N^+ - CH_2$], 69 (100) [$C_4H_7N^+$]; correct elemental analysis.

[8] Crystal data for **3a**: $C_{20}H_{36}Cl_2N_2P_2$, $M_r = 437.4$, orthorhombic, space group $P2_12_12_1$ (no. 19), colorless crystals, dimensions $0.50 \times 0.18 \times 0.13$ mm^3, $a = 11.078(1)$, $b = 14.570(2)$, $c = 14.596(1)$ Å, $V = 2355.9(4)$ Å^3, $\rho_{calcd} = 1.233$ Mg m^{-3}, $Z = 4$, $\mu(Cu_{K\alpha}) = 3.81$ mm^{-1}, $T = 200(2)$ K; of 5327 reflections collected, 3833 were symmetry-independent and used for the structure solution (direct methods)[9a] and refinement (full-matrix least squares on F^2, 236 parameters).[9b] Non-hydrogen atoms were refined anisotropically, and H atoms localized by difference electron density and refined with a riding model ($wR2 = 0.136$, $R1 = 0.051$, for $I > 2\sigma(I)$). An empirical absorption correction on the basis of ψ scans was applied; the absolute structure could not be determined reliably. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100757. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[14] See also a) G. Wu, R. E. Wasylishen, R. D. Curtis, *Can. J. Chem.* **1992**, *70*, 863; b) K. Eichele, G. Wu, R. E. Wasylishen, *J. Magn. Reson. A* **1993**, *101*, 157, and references therein. Under consideration of the limitations outlined in ref. [13a], the following principal values of the phosphorus shielding tensors were obtained from the MAS spectra: **2a**: $\delta_{11} = 150$, $\delta_{22} = 85$, $\delta_{33} = -181$; **3a**: $\delta_{11} = 170$, $\delta_{22} = 72$, $\delta_{33} = -185$.

[15] The energy optimation at the MP2 level was performed with the Gaussian set of programs: Gaussian 94 (Revision D4), M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, Gaussian Inc., Pittsburgh, PA, **1995**.

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[17] All stationary points on the electronic hypersurface were characterized by vibrational analysis based on the method of numerical differentiation of the first-order gradients. Consequently, energy minima possess overall positive vibrational frequencies, and the two transition states display one imaginary vibration. Energy values were obtained from the MCSCF energies after zero-point vibrational correction.

[18] A stable phosphanylcarbene is known;[19] intermediates of this type are also supposed to appear in the thermal rearrangement of 1,3-diphosphacyclobutane-2,4-diyl **2b** to an isomeric 1,3-diphosphapropene.[4]

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Intense Dyes through Chromophore–Chromophore Interactions: Bi- and Trichromophoric Perylene-3,4:9,10-bis(dicarboximide)s**

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Dedicated to Professor Heinrich Nöth on the occasion of his 70th birthday

The UV/Vis spectra of dyes have commonly been controlled by introducing suitable substituents or by altering the chromophore. An interesting alternative is allowing two or more identical chromophores to interact directly, which might be expected to give pronounced effects in color. Perylene-3,4:9,10-bis(dicarboximide)s **1** were chosen as the basic chromophore because of their unusually high chemical and photochemical persistency and their high fluorescent quantum yields.[1] Moreover, the absorption of **1** in the visible region is caused by only one electronic transition,[2] and there are orbital nodes[3] at the nitrogen atoms in the HOMO and LUMO, which make these atoms ideal positions for linking. The thus "closed chromophore" is only negligibly influenced by substituents. The linking of two chromophores of **1** through a longer spacer did not result in a considerable alteration of the UV/Vis spectra.[4–6] Only an appreciable overlap of the chromophors induced a strong exciton absorption at longer wavelengths.[7, 8]

Here we try to adjust the chromophore–chromophore interaction to just an exciton coupling by reducing the separation between two chromophores to the distance of a single bond. Undesired interaction between the chromophores through conjugation is excluded by their orthogonal orientation and linkage at the nitrogen atoms (orbital nodes).

The starting material for the synthesis of such polychromophores are the peryleneimides **3**, which are readily soluble and have a free amino group at one nitrogen atom. Compounds **3**-

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