Odd-Electron Bonds

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Dimerization of a Cyclo-1σ^4,3σ^2,4σ^2-Triphosphapentadienyl Radical: Evidence for Phosphorus–Phosphorus Odd-Electron Bonds**

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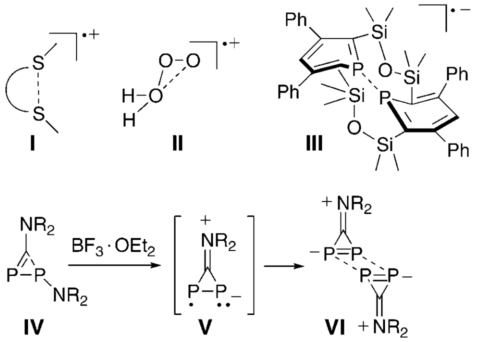
Dedicated to Professor Herbert Roesky
on the occasion of his 70th birthday

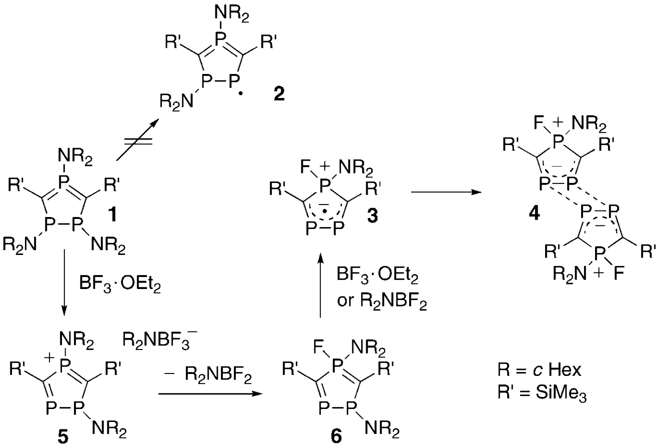
In hydrocarbon chemistry, carbon-centered radicals are rather short-lived intermediates and usually dimerize to give classical two-electron bonds.[1] If main group elements are involved, however, the situation is more diverse;[2] as predicted as early as 1931 by Pauling,[3] odd-electron bonds are sometimes formed. For Group 16 elements, the intensely studied radical cations of type **I**[4] are a good illustration of compounds that feature a two-center, three-electron bond, in which two electrons occupy a σ bonding orbital, and one electron occupies a σ* antibonding orbital (Scheme 1). Three-center, one-electron bonds have also been evoked to rationalize the formation of radical cation **II**;[5] in this case, the singly occupied π* orbital of O_2^+ interacts with an electron lone-pair orbital on water.



Scheme 1. Some examples of compounds that feature odd-electron bonds, and the synthetic route from **IV** to **VI**.

In phosphorus chemistry, only two examples of compounds that feature odd-electron bonds are known. Le Floch and co-workers[6] prepared the macrocyclic derivative **III**, which features a two-center, one-electron P–P bond in which the single electron is mainly located in a P–P σ bonding orbital. In 1998, we isolated derivative **VI**, which features a P_4 framework, which is best described as a four-center, six-π-electron system.[7] Four π electrons are present in the π orbitals of the two P=P bonds within each CP_2 ring, and the remaining two π electrons are used to join the two CP_2 units by two two-center, one-electron bonds. This description is consistent with the observation that the intra-ring P–P bonds are quite short (2.205 Å), whereas the inter-ring P–P bonds are very long (2.634 Å). Derivative **VI** resulted from the π*-π* dimerization[8] of diphosphirenyl radical **V**. Indeed, according to calculations, the unpaired electron of **V** is equally distributed over both phosphorus atoms and is localized in the π* orbital of the P=P bond.

In an attempt to prepare radical **2**, in which the unpaired electron would be distributed over a more extended π-conjugated framework, cyclic bis(methylene)phosphorane **1**[9] was treated with $BF_3{\cdot}OEt_2$ in a method used to homolytically cleave the P–N bond of diphosphirene **IV**. After removal of all the volatiles under vacuum and extraction with pentane, a new compound **4** was obtained in 40 % yield as an air-sensitive purple solid (Scheme 2). Surprisingly, the ^{31}P NMR spectrum showed a doublet of triplets at $\delta = 89$ ppm ($J_{P,F} = 938$ Hz and $J_{P,P} = 18$ Hz), characteristic of tetracoordinate phosphorus bearing a fluorine atom. It also had a very broad signal around 300 ppm in the region of phosphaalkene moieties. ^{19}F NMR spectroscopy gave a signal at $\delta = 23$ ppm as a doublet of triplets ($J_{F,P} = 938$ Hz and $J_{F,P} = 7$ Hz). The large P–F coupling constant confirms the direct P–F bond, and the triplet multiplicity of the signal is in good agreement with the presence of a P–P fragment. In solution at room temperature, no trace of paramagnetic species was detected by ESR spectroscopy.



Scheme 2. The synthesis of derivative **4**. *c*Hex = cyclohexyl.

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Dissolving **4** in hot toluene ($\approx 60\,°C$) followed by slow cooling of the solution gave deep-red crystals suitable for a single-crystal X-ray diffraction study (Figure 1).[10] Compound **4** is organized around an inversion center located in the middle of the parallelogram described by four phosphorus atoms (P–P–P angles: 97.2° and 82.7°). The plane of the parallelogram is almost perpendicular (109 and 112°) to the two planar five-membered rings. All C–P bond lengths in the latter are equal (1.70 Å) and only slightly longer than C=P double bonds. The distance between the two five-membered rings of **4** is 2.427 Å, which is much longer than a classical P–P single bond,[11] but almost 0.2 Å shorter than that of the diphosphirenyl radical dimer **VI** (2.635 Å). In contrast, the P2–P3 bond length is short (2.157 Å), in fact even shorter than the analogous bond in **VI** (2.205 Å).

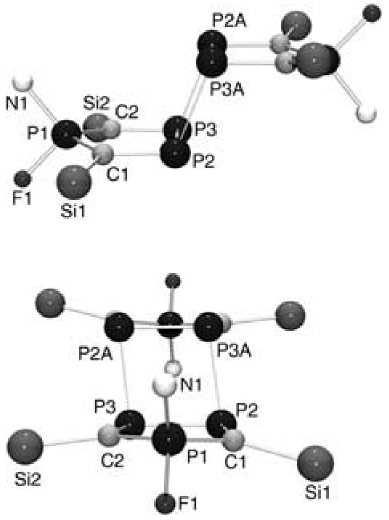


Figure 1. Simplified molecular views of **4** in the solid state. Selected bond lengths [Å] and angles [°]: P2–P3A 2.427(3), P1–C1 1.700(7), P1–C2 1.693(7), C1–P2 1.698(7), C2–P3 1.700(7), P2–P3 2.157(3), P1–N1 1.656(6), P1–F1 1.562(4), C1–Si1 1.851(7), C2–Si2 1.864(3); ∢C1-P1-C2 107.7(3), ∢P1-C1-P2 115.1(4), ∢P1-C2-P3 116.4(4), ∢C1-P2-P3 100.8(3), ∢C2-P3-P2 98.9(3), ∢P1-C1-Si1 128.6(4), ∢P2-C1-Si1 116.2(4), ∢P2-P3-P2A 82.7(11), ∢P3-P2-P3A 97.2(11), ∢$_{tors}$C1-P2-P3-P2A 109.1, ∢$_{tors}$C2-P3-P2-P3A 112.4.

Before performing a detailed investigation of the electronic structure of **4**, we studied the reaction leading to this unexpected compound. ^{31}P and ^{19}F NMR spectroscopy indicated that a small amount of cyclic ylide **6** was formed (Scheme 2). This compound was isolated by crystallization in THF, and its structure was unambiguously established by a single-crystal X-ray diffraction study (Figure 2).[10] Hence, it is reasonable to postulate that instead of the expected homolytic cleavage of a P–N bond, which would have led to **2**, heterolytic cleavage occurs to generate a cyclic methylenephosphonium salt **5**, as already observed by Grützmacher and Pritzkow in their work with analogous acyclic compounds.[12] The highly electrophilic cation **5** then abstracts a fluorine anion from the $R_2NBF_3^-$ counteranion to give the isolated cyclic ylide **6**. Finally, BF_3-catalyzed homolytic cleavage of the remaining σ^3-P–N bond leads to the transient cyclotriphosphapentadienyl radical **3**, which dimerizes to give **4**. Therefore, although we have not generated the desired radical **2**, we have, by serendipity, formed the radical **3** in which the unpaired electron is distributed over an extended π-conjugated framework, which was our primary aim.

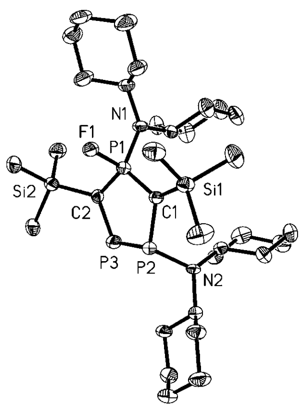


Figure 2. Molecular view of **6** in the solid state. Selected bond lengths [Å] and angles [°]: P1–C1 1.686(4), P1–C2 1.764(4), P2–C1 1.772(4), P3–C2 1.708(4), P2–P3 2.159(2), P1–N1 1.657(3), P1–F1 1.508(2), P2–N2 1.685(3), C1–Si1 1.854(4); ∢C1-P1-C2 109.0(2), ∢P1-C1-P2 111.5(2), ∢P2-P3-C2 97.2(1), ∢P1-C2-P3 116.0(2).

The single occupied molecular orbital (SOMO) of radicals of type **3** is, upon first estimate, the π_3 molecular orbital of a *cis*-oriented pentadiene unit with small contributions from the PR_2 fragment (Figure 3). Among the three symmetry-allowed dimerization processes that could occur from SOMO–SOMO (π_3–π_3) interactions, the [2+2] pathway clearly leads to the least sterically hindered and minimally strained product, namely **4**. In terms of canonical structures, radicals **3** can be represented as follows: the unpaired electron can reside at the carbon positions, as in **A**, or at the phosphorus atoms, as indicated in **B** (Scheme 3). As a consequence, a double bond is present between either the two phosphorus atoms (in **A**), or a phosphorus and a carbon atom (in **B**). From **A**, dimerization refers to a [π^2+π^2] reaction of two P=P double bonds and would result in a cyclotetraphosphane ring system with four

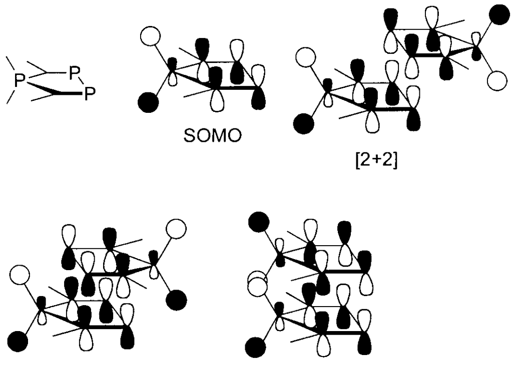
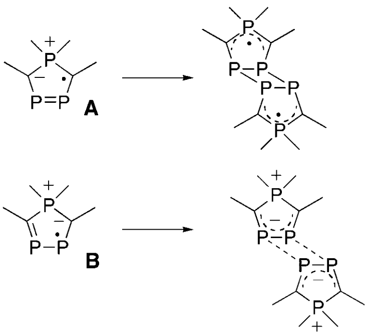


Figure 3. Representation of the SOMO for radical **3** and possible SOMO–SOMO interactions.



Scheme 3. Canonical structures **A** and **B** for radical **3** and the respective canonical structures for the product dimer **4**.

P–P single bonds.[13] However, for the dimerization from **B**, only one unpaired electron is supplied from each radical unit. This results in an electron deficit for the resulting inter-ring P–P bonds, as only two electrons are available for forming two P–P bonds. The presence of the resonance form **A** in competition with **B** easily explains the differences observed in the P–P bond lengths between the four-membered-ring framework of dimers **VI** and **4**, and especially why the "long" P–P bond is shorter in **4**.

Another consequence of these two alternative resonance structures would be the ability to vary the P–P bond lengths in dimers of type **4** by changing the substituents attached to the carbon atoms. To substantiate these qualitative considerations, we performed quantum chemical calculations (Table 1). Various computational levels[14] were tested for the parent compound ($R^1 = R^2 = H$). Given the same DFT level (BP86) and increasing the quality of the basis set in the order SVP, TZVP causes only a slight shortening of the long P–P bonds. On the other hand, changing the electron correlation level from BP86 to MP2 exerts a stronger shrinking of the P–P bonds. The CBS-Q method (complete basis set method), considered to be a much better computational level,[14b] yields, for the parent dimer, a long inter-ring P–P distance of 2.592 Å and a concomitant dimerization energy of $-19.6\,\text{kcal}\,\text{mol}^{-1}$ (0 K). The effects of the different substituents were investigated with the less costly computational level (RI-BP86/SVP). Not surprisingly, the substituents at the carbon atoms which stabilize the canonical structure **A** and the electronegative substituents at phosphorus, shorten the inter-ring P–P distance. A drastic shortening is observed with an added exchange of substituents that can simultaneously stabilize a negative charge and an unpaired electron ($R^1 = NO_2$, SiH_3; $R^2 = F$). In contrast, strong electron-donating substituents at the carbon atoms, such as amino groups, elongate the inter-ring P–P distance. In all cases, a rhombic distortion of the central P_4 ring is observed. For the experimentally observed derivative (R^1 = TMS; R^2 = F or N(*c*Hex)$_2$), the calculated inter-ring P–P distance (2.599 Å) is still too large to agree well with the experimentally determined value of 2.427 Å; this probably means that DFT methods are not able to take weak bonds into account properly.[15]

Table 1: Substituent effects on P–P bond lengths and P-P-P bond angles for dimers of type **4** at the RI-BP86/SVP level.

R^1 (C)	R^2 (P)	P–P$_{\text{interring}}$ [Å]	P–P$_{\text{intraring}}$ [Å]	∢ P-P-P [°]
H	H	2.702	2.220	87.8
		2.676[a]	2.221[a]	86.8[a]
		2.614[b]	2.215[b]	80.2[b]
		2.592[c]	2.209[c]	77.8[c]
		2.538[d]	2.222[d]	77.4[d]
NH_2	H	2.754	2.218	89.9
CH_3	H	2.718	2.214	89.8
SiH_3	H	2.635	2.226	82.3
phenyl	H	2.576	2.213	89.4
H	NH_2	2.655	2.241	88.7
H	F	2.588	2.255	89.9
NH_2	F	2.641	2.256	89.9
SiH_3	F	2.535	2.256	89.9
NO_2	F	2.484	2.258	83.2
SiH_3	F[f]/NH_2[g]	2.520	2.256	84.2
		2.473[b]	2.258[b]	79.1[b]
SiH_3	NH_2[f]/F[g]	2.550	2.252	84.9
		2.481[b]	2.254[b]	80.2[b]
TMS[e]	F[f]/N(*c*Hex)$_2$[g]	2.599	2.229	87.1
TMS[e]	N(*c*Hex)$_2$[f]/F[g]	2.601	2.247	88.0

[a] RI-BP86/TZVP; [b] RI-MP2(fc)/SVP; [c] CBS-Q (complete basis set method)[14]; [d] RI-MP2(fc)/TZVP; [e] TMS = trimethylsilyl; [f] *exo* with respect to the central four-membered-ring system; [g] *endo* with respect to the central four-membered-ring system.

A series of radical dimers of type **4** that feature different substituents at phosphorus and carbon positions are under current investigation. The possibility of finely tuning the interaction between such radicals might have implications in material sciences.[16]

Experimental Section

All manipulations were performed under an inert atmosphere of argon by using standard Schlenk techniques. Dry, oxygen-free solvents were employed. ^1H, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded on Bruker AC80, AC200, WM250 or AMX400 spectrometers.

4: $BF_3{\cdot}Et_2O$ (0.24 g, 1.30 mmol) was added at room temperature to a solution of **1** (0.45 g, 0.62 mmol) in toluene. The solution was heated at 30 °C for 2 days in the absence of light, and the reaction monitored by multinuclear NMR spectroscopy. When the starting materials were consumed, the volatiles were removed under vacuum and the product was extracted with toluene. After evaporation of toluene, the residue was recrystallized from hot toluene as deep-red crystals (0.12 g, 42 %); m.p. = 115 °C (decomp); $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = 88.9$ (dt, $^2J(P,P) = 15.3$ Hz, $^1J(P,F) = 939.8$ Hz, 1P), 280 ppm (br, 2P); ^1H NMR (C_6D_6): $\delta = 0.78$ (s, 36H, $SiCH_3$), 1.2–2.2 (m, 20H, CH_2), 3.04 (br, 4H, CHN), 3.65 ppm (broad d, $^2J(P,H) = 13.8$ Hz, 4H, CHN); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 3.9$ (s, $SiCH_3$), 25.5, 25.8, 26.7, 27.1 (s, CH_2), 34.3 (br, CH_2), 35.1 (d, $^2J(C,P) = 1.3$ Hz, CH_2), 57.4 (broad, NCH), 58.2 ppm (d, $^2J(C,P) = 5.1$ Hz, NCH), PCP (not observed); $^{19}F\{^1H\}$ NMR (C_6D_6): $\delta = 20.1$ ppm (dt, $^3J(F,P) = 60.0$ Hz, $^1J(F,P) = 939.8$ Hz). Computational procedures: quantum chemical calculations were performed with the Gaussian suite[14a] of programs as well as the Turbomole[14b] program systems. Various computational levels were studied. In general, RHF and B3LYP calculations yielded intermolecular bond lengths that were too large, whereas the BP86 density functional level yielded more satisfactory geometries, albeit with some P–P bond lengths too large for intermolecular bond formation between two radicals. At the MP2 level, shorter P–P bonds were observed, but this methodology is restricted to the study of the parent compound.

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[1] M. Newcomb in *Reactive Intermediate Chemistry* (Eds.: M. Jones, R. A. Moss), Wiley-Interscience, Hoboken, **2004**, pp. 121–164.

[2] H. Grützmacher, F. Breher, *Angew. Chem.* **2002**, *114*, 4178; *Angew. Chem. Int. Ed.* **2002**, *41*, 4007.

[3] L. Pauling, *J. Am. Chem. Soc.* **1931**, *53*, 3225; L. Pauling, *The Nature of the Chemical Bond, 3rd ed.*, Cornell University Press, Cornell, **1960**, pp. 340–343.

[4] R. S. Glass, *Top. Curr. Chem.* **1999**, *205*, 1; D. K. Maity, *J. Am. Chem. Soc.* **2002**, *124*, 8321; J. E. King, A. J. Illies, *J. Phys. Chem. A* **2004**, *108*, 3581.

[5] M. Zhou, A. Zeng, Y. Wang, Q. Kong, Z.-X. Wang, P. von R. Schleyer, *J. Am. Chem. Soc.* **2003**, *125*, 11512.

[6] L. Cataldo, S. Choua, T. Berclaz, M. Geoffroy, N. Mézailles, L. Ricard, F. Mathey, P. Le Floch, *J. Am. Chem. Soc.* **2001**, *123*, 6654.

[7] Y. Canac, D. Bourissou, A. Baceiredo, H. Gornitzka, W. W. Schoeller, G. Bertrand, *Science* **1998**, *279*, 2080.

[8] Although dimer **VI** is the only example of a phosphorus compound resulting from a π^*-π^* interaction, such interactions have been found in numerous inorganic molecules: a) T. Klapötke, J. Passmore, *Acc. Chem. Res.* **1989**, *22*, 234; b) J. M. Rawson, A. J. Banister, I. Lavender, *Ad. Heterocycl. Chem.* **1995**, *62*, 341; c) J. Beck, *Coord. Chem. Rev.* **1997**, *163*, 55; d) T. Drews, W. Koch, K. Seppelt, *J. Am. Chem. Soc.* **1999**, *121*, 4379; e) S. Brownridge, I. Krossing, J. Passmore, H. D. B. Jenkins, H. K. Roobottom, *Coord. Chem. Rev.* **2000**, *197*, 397.

[9] T. Kato, Dissertation Thesis Université Paul Sabatier, Toulouse, **2002**.

[10] Crystal data: **4**: $C_{20}H_{40}FNP_3Si_2$, $M = 462.62$, monoclinic, $P2_1/n$, $a = 11.192(4)$ Å, $b = 17.994(6)$ Å, $c = 12.621(5)$ Å, $\beta = 99.563(7)°$, $V = 2506.2(15)$ Å^3, $Z = 4$, $T = 193(2)$ K. 8658 reflections (3061 independent, $R_{int} = 0.1249$) were collected. Largest electron density residue: 0.379 e Å^{-3}, R_1 (for $I > 2\sigma(I)) = 0.0709$ and $wR_2 = 0.1411$ (all data) with $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = (\Sigma w\,(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2)^{0.5}$. **6**: $C_{32}H_{62}FN_2P_3Si_2$, $M = 642.93$, orthorhombic, *Pbca*, $a = 12.399(1)$ Å, $b = 21.421(1)$ Å, $c = 27.409(2)$ Å, $V = 7279.9(8)$ Å^3, $Z = 8$, $T = 193(2)$ K. 25920 reflections (4589 independent, $R_{int} = 0.1183$) were collected. Largest electron density residue: 0.257 e Å^{-3}, R_1 (for $I > 2\sigma(I)) = 0.0454$ and $wR_2 = 0.0910$ (all data). All data for the structures represented herein were collected at low temperatures with an oil-coated shock-cooled crystal on a Bruker-AXS CCD 1000 diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods[17] and all non-hydrogen atoms were refined anisotropically by using the least-squares method on F^2.[18] CCDC 269192 (for **4**) and CCDC 269193 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[11] H. F. Allen, O. Kennard, D. G. Waston, L. Brammer, A. Orpen, *J. Chem. Soc. Perkin Trans. 2* **1987**, S1.

[12] H. Grützmacher, H. Pritzkow, *Angew. Chem.* **1989**, *101*, 768; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 740.

[13] Such a $[\pi^2 + \pi^2]$ reaction of two P=P double bonds has already been observed for a 3H-diphosphirene. E. Niecke, R. Streubel, M. Nieger, *Angew. Chem.* **1991**, *103*, 103; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 90.

[14] a) GAUSSIAN 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakasuji, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**; b) TURBOMOLE, Program Package for ab initio Electronic Structure Calculations, Version 5.7, R. Ahlrichs, M. Bär, H.-P. Baron, R. Bauernschmitt, S. Böcker, M. Ehrig, K. Eichkorn, S. Elliott, F. Furche, F. Haase, M. Häser, C. Hättig, H. Horn, C. Huber, U. Huniar, M. Kattannek, A. Köhn, C. Kölmel, M. Kollwitz, K. May, C. Ochsenfeld, H. Öhm, A. Schäfer, U. Schneider, O. Treutler, K. Tsereteli, B. Unterreiner, M. von Arnim, F. Weigend, P. Weis, H. Weiss, Theoretical Chemistry Group, University of Karlsruhe, Karlsruhe, Germany, **2004**.

[15] The diamagnetic coupling of two radicals through π^*–π^* interactions usually leads to weak bonds. Consequently, the bond lengths in these dimers easily fluctuate. This is well-documented for the N_2O_2 dimer. For example, the N–N interatomic distance in the gas phase[15a] is 2.24 Å, whereas it is 2.18 Å in the solid state.[15b] a) S. G. Kukolich, *J. Am. Chem. Soc.* **1982**, *104*, 4715; b) W. N. Lipscomb, W. R. Wang, *Acta Cryst.* **1961**, *14*, 1100.

[16] M. E. Itkis, X. Chi, A. W. Cordes, R. C. Haddon, *Science* **2002**, *296*, 1443.

[17] G. M. Sheldrick, *Acta Cryst.* **1990**, *46*, 467.

[18] SHELXL 97, Program for Crystal Structure Refinement, G. M. Sheldrick, University of Göttingen **1997**.