Cyclophane Structure and Behavior

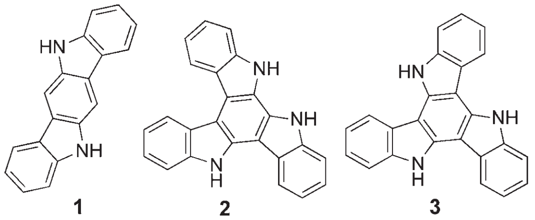
DOI: 10.1002/ange.200600526

A Redox-Active C_3-Symmetric Triindole-Based Triazacyclophane**

Berta Gómez-Lor, Gunther Hennrich, Beatriz Alonso, Angeles Monge, Enrique Gutierrez-Puebla, and Antonio M. Echavarren**

Interest in carbazole-based compounds has grown over the last few years due to their photoconductive properties and ability to transport positive charges (holes). Many carbazole-containing polymers and oligomers have been synthesized for electronic applications.[1] In fields like nonlinear optics, xerography, photorefractives, and organic light-emitting diodes, the photoconductivity or hole-transport properties of the carbazolyl groups are being extensively utilized.[2] In addition, new carbazole-related molecules such as indolo[3,2-*b*]carbazole (**1**)[3] and 6,11-dihydro-5*H*-diindolo[2,3-*a*;2′,3′-*c*]carbazole (**2**)[4] have been prepared which show extended π systems in which two or three carbazole units, respectively, share an aromatic ring (Scheme 1). These structures are being widely investigated in the field of organic electronics.

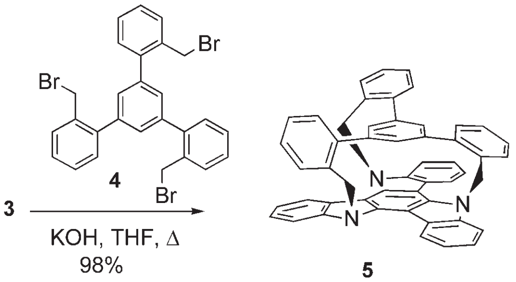
In contrast to compound **2**, which is easily obtained by oxidative trimerization of indole, the symmetrical analogue 10,15-dihydro-5*H*-5,10,15-triazadiindeno[1,2-*a*;1′,2′-*c*]fluorene (**3**) has been very rarely studied, probably due to difficulties in its synthesis.[5] Owing to its extended π system and its planar, disk-like structure, this C_3-symmetric molecule offers great potential as a central core for the construction of columnar liquid crystals for one-dimensional conduction.[6] We have recently reported the convenient synthesis of **3**[7] from a known symmetrical hexabromotriindole[8] by palladium-catalyzed reductive debromination with triethylammonium formate. The ready availability of **3** on the multigram scale prompted us to investigate the electron-donating nature of this platform.



1 **2** **3**

Scheme 1. Carbazole-based molecules with extended π systems.

Herein we report on the high-yielding synthesis of a new triazacyclophane based on this triindole platform, its crystal structure and redox behavior, and the characterization by X-ray diffraction of the corresponding radical cation. Triindole platform **3** is *N*-alkylated in order to avoid N–N coupling, which is one of the undesired chemical side reactions that can cause irreversible cyclic voltammetry behavior of carbazole derivatives upon oxidation. The alkylation of **3** with tris(benzylbromide)benzene **4** was performed with the aim to get a cyclophane as their unique geometry forces the aromatic rings into a cofacial arrangement that makes them perfect models for charge-transport processes.[9] Triazacyclophane **5** was obtained as a white powder in almost quantitative yield (Scheme 2).[10]



Scheme 2. Synthesis of cyclophane **5**.

Recrystallization of **5** from $CHCl_3$ furnishes colorless crystals suitable for X-ray diffraction. The X-ray crystal structure determination indicates that the central rings of the triindole and the triphenylbenzene are practically parallel (0.7(4)°) and are held at a distance of 3.223(4) Å, with the central benzene units being slightly rotated ($\approx 9°$) with respect to each other (Figure 1). The molecules of **5** pack in the crystal in pairs of enantiomers, isolated by solvent molecules, with a staggered face-to-face arrangement of the triphenylbenzene moiety (distance between the centroids of the central ring: 5.787(4) Å). Crystallographic packing (Figure 2) shows no evidence for a triindole/triindole interaction.

Cyclophane **5** shows NMR data consistent with C_3 symmetry (Figure 3a). As a result of the rigid structure, the methylene hydrogen atoms appear as AX systems with a coupling constant of $J = 14.7$ Hz. Unequivocal ^1H NMR signal assignments were made on the basis of COSY and HMQC experiments. Addition of trifuoroacetic acid (TFA) to the $CDCl_3$ solution yielded a dark-blue solution, for which all the NMR signals except H6–H9 are broadened or have even

---

[*] Dr. B. Gómez-Lor, Prof. Dr. A. Monge, Prof. Dr. E. Gutierrez-Puebla
Instituto de Ciencia de Materiales de Madrid
Cantoblanco, 20849 Madrid (Spain)
Fax: (+34) 91-372-0623
E-mail: bgl@icmm.csic.es
Prof. Dr. A. M. Echavarren
Institut Català d'Investigació Química (ICIQ)
43007 Tarragona (Spain)
Fax: (+34) 97-792-0218
E-mail: aechavarren@iciq.es
Dr. G. Hennrich, Dr. B. Alonso
Departamento de Química Orgánica
Departamento de Química Inorgánica
Universidad Autónoma de Madrid
Cantoblanco, 20849 Madrid (Spain)

[**] We are grateful to the Ministerio de Educación y Ciencia (MEC; grant nos. CTQ2004-02865/BQU to B.G.-L. and CTQ2004-02869 to A.M.E. and Ramón y Cajal contract to G.H.), the Comunidad Autónoma de Madrid (project no. 200580M133), and the ICIQ Foundation for financial support. We also thank Prof. J. Elguero for helpful comments.

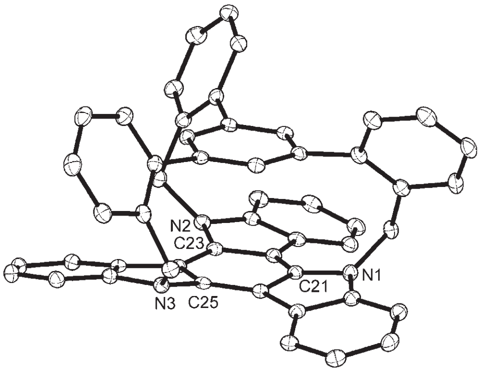


Figure 1. ORTEP plot of **5**.

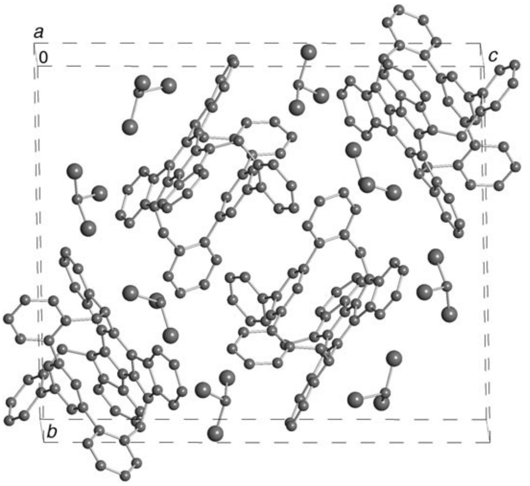


Figure 2. Unit cell of **5**–$(CHCl_3)_2$.

vanished (Figure 3b).[11] TFA has been used as a one-electron oxidant to generate radical cations,[12] even though there is controversy about how the oxidation actually occurs.[13] The broadening of the proton signals is presumably due to fast electron exchange between the radical cation and the neutral parent molecule, and it reveals the electron spin density on the different sites of the radical cation. Broadening of the H10 NMR signal therefore suggests a spin delocalization through space.

From oxidized solutions of **5**, black crystals suitable for X-ray crystallography were obtained; these crystals are surprisingly stable at room temperature for several weeks. X-ray analysis indicates the structure to be the dimeric radical cation $(\mathbf{5})_2^{\bullet+}$, with the positive charge delocalized over the two molecules within the dimeric structure[14,15] and with two disordered hydrogen-bonded trifluoroacetate molecules acting as counterions for each dimer.[16] Related trifluoroacetate dimers have been previously reported as counterions.[17] The crystal packing shows infinite stacks in which two cyclophane enantiomers are in a staggered face-to-face arrangement of the triindole moieties, with a separation of 3.270(4) Å (centroid–centroid distance of the central rings), isolated by the anions (Figure 4). The close distance, shorter than the sum of normal van der Waals separation, is also indicative of the formation of discrete radical cation dimers.

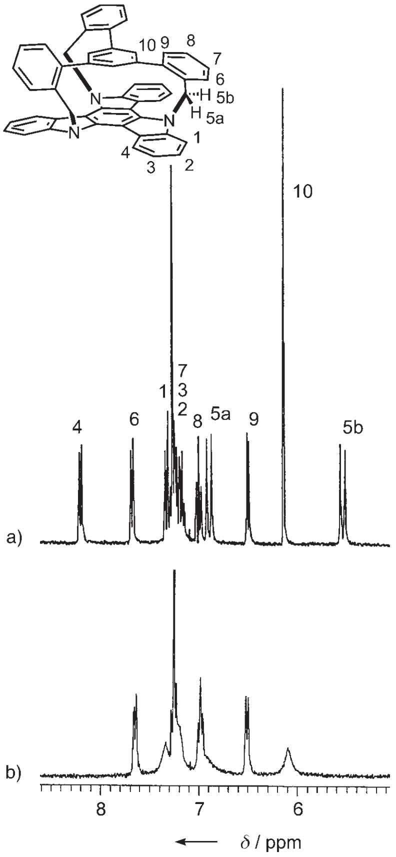


Figure 3. NMR signals for cyclophane **5** a) before and b) after addition of TFA.

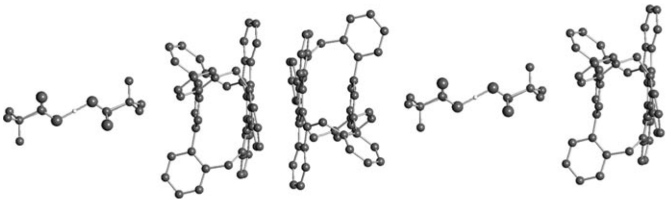


Figure 4. Alternation of the dimeric stacks of $(\mathbf{5})_2^{\bullet+}$ and the anions $(CF_3COO^-{\cdot}CF_3COOH)$ along the direction (111).

These dimers are considered to be the smallest supramolecular unit that can carry a delocalized positive charge.[14b,18]

Structure comparison of the neutral and the radical-cation dimers shows some differences, in spite of the molecular strain of cyclophane **5**. The most notable difference is a shortening in the distance between the central rings of the triindole and the triphenylbenzene (3.169(4) Å in the radical cation), thereby suggesting a through-space interaction. Another difference is the contraction of the bonds connecting each nitrogen atom with the central benzene ring in the radical cation (N1–C21 1.377(4), N2–C23 1.394(4), N3–C25 1.376(4) Å) relative to those in the neutral donor (N1–C21 1.397(3), N2–C23 1.407(3), N3–C25 1.392(3) Å). This reflects delocalization of the charge over the triindole platform. No other remarkable geometrical changes were observed.

The chemical oxidation of **5** was monitored by UV/Vis spectroscopy. Upon addition of phenyliodine(III) bis(trifluoroacetate) (PIFA) to a solution of **5** in CH_2Cl_2, dramatic changes occur in three spectral regions (Figure 5). Diminution of the major triindole absorption (306 nm) is accompanied by an increase of two bands in the visible region (412 (minor) and 682 nm (major)) and the appearance of a broad, weak band in the near infrared (900–1030 nm). The spectral changes are time-dependent and are completed after 15 min under the chosen experimental conditions.

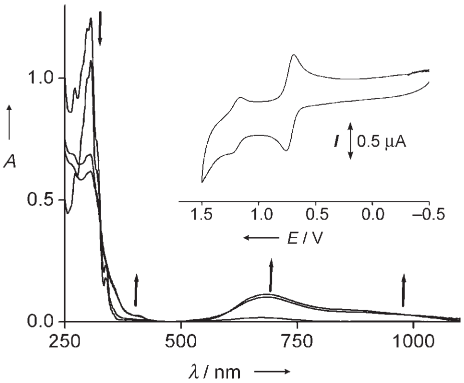


Figure 5. Change in the UV/Vis absorption of **5** in CH_2Cl_2 ($c = 10^{-5}$ mol L^{-1}) upon addition of PIFA (10 equiv), after 0.5, 10, and 15 min. Inset: Cyclic voltammogram of **5** ($c = 10^{-5}$ mol L^{-1}) recorded in CH_2Cl_2/0.1 M tetra-*n*-butylammonium hydroxide (TBAH) with a Pt working electrode. Scan rate: 0.1 V s^{-1}.

We attribute these changes to the formation of a radical cation species with characteristic absorption in the visible region.[19] The radical species would immediately form a dimeric charge-resonance (CR) complex between the initially formed radical cation and its neutral counterpart, thereby yielding a distinctive CR band in the near infrared.[20] The coexistence of all three species (the neutral, monomeric radical cation, and CR complex species) gives rise to a complex absorption spectrum with broad, overlapping bands. The time dependence of the formation of the new species is influenced by the oxidation agent used, as demonstrated for comparable systems.[21] However, the spectra observed after 15 min remain practically unchanged for hours, a result that indicates the stability of the generated radical and complex species.

Cyclic voltammograms of **5** show two well-defined reversible redox processes at 0.8 and 1.2 V (Figure 5, inset). Interestingly, the anodic peak current of the second wave is lower than the i_p value of the first oxidation step and is concentration-dependent, decreasing as the effective concentration of **5** lowers, most likely due to the formation of dimeric assemblies, as shown previously.

In conclusion, a novel triazacyclophane, **5**, based on the C_3-symmetric indole trimer **3**, that forms unusually stable radical cation–neutral molecule dimers upon oxidation has been synthesized. X-ray evaluation of the differences in the structure of the neutral and oxidized species has been achieved; this is usually a difficult task due to the characteristic instability of radical species. This crystallographic study revealed a dimeric association of $(\mathbf{5})_2^{\bullet+}$ through the triindole platform. In solution, the presence of the radical species, forming dimeric resonance-transfer complexes, is confirmed by employing UV/Vis spectroscopy. The intriguing structural and electronic properties of the novel cyclophane reported herein hold great promise for potential applications of trindole-based materials in the field of molecular electronics. Research in this direction is ongoing.

Experimental Section

X-ray structure determinations: Colorless crystals of **5** and dark-blue crystals of $\mathbf{5}^{\bullet+}$ showing well-defined faces were mounted on a Bruker-Siemens Smart CCD diffractometer equipped with a low-temperature device, a normal focus, and a 2.4-kW sealed-tube X-ray source ($Mo_{K\alpha}$ radiation, $\lambda = 0.71067$ Å) operating at 50 kV and 20 mA. Low-temperature data (173 K) were collected over a hemisphere of the reciprocal space by a combination of three exposure sets. Each exposure of 10 s covered 0.3° in ω over the ranges $2° < \theta < 29°$ (for **5**) and $2° < \theta < 27°$ (for $\mathbf{5}^{\bullet+}$).The first 100 frames were recollected at the end of the data collection to monitor crystal decay. The intensities were corrected for Lorentz and polarization effects. The structures were solved by the Multan and Fourier methods. Crystal data for **5**–$(CHCl_3)_2$: crystal dimensions: $0.20 \times 0.20 \times 0.16$ mm^3; unit cell dimensions: $a = 10.710(1)$, $b = 18.399(2)$, $c = 21.948(3)$ Å; monoclinic, space group $P2(1)/c$, $\beta = 99.948(2)°$, $V = 4259.9(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.445$ mg m^{-3}. **5**–$(CHCl_3)_2$ was refined anisotropically: $R1(F) = 0.1021$ for all data; $R1(F) = 0.0771$ for observed data with $I > 2\sigma(I)$; GOF(F2) = 1.10. Crystal data for $(\mathbf{5})_2^{\bullet+}$–$(CF_3COO^-{\cdot}CF_3COOH)$: crystal dimensions: $0.20 \times 0.20 \times 0.20$ mm^3; unit cell dimensions: $a = 12.1969(6)$, $b = 12.4372(6)$, $c = 13.0011(6)$ Å; triclinic, centrosymmetric space group $P\bar{1}$, $\alpha = 80.570(1)$, $\beta = 81.874(1)$, $\gamma = 83.194(1)°$, $V = 1916.8(2)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.388$ mg m^{-3}. $(\mathbf{5})_2^{\bullet+}$–$(CF_3COO^-{\cdot}CF_3COOH)$ was refined anisotropically: $R1(F) = 0.1060$ for all data; $R1(F) = 0.0851$ for observed data with $I > 2\sigma(I)$; GOF(F2) = 1.06. The trifuoracetate groups are disordered and a model of disorder of the α carbon atoms was employed. The typical CF_3 disorder is also present but attempts to model it did not improve the refinement process. Most of the calculations were carried out with SMART[22] software for data collection and reduction and the SHELXTL[23] software for structure solution and refinements. CCDC 297289 and CCDC 297290 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.

Cyclophane **5**: A mixture of **3** (102 mg, 0.3 mmol) and KOH (168 mg, 3 mmol) in THF (40 mL) was heated under reflux for 15 min. Tribromide **4** (176 mg, 0.3 mmol) was then added and the mixture was heated for 16 h. The mixture was diluted with EtOAc, washed with 10 % aqueous HCl and saturated aqueous NaCl solution, dried (Na_2SO_4), and evaporated. The residue was purified by chromatography with CH_2Cl_2/hexanes (1:1) to give **5** as a white solid (200 mg, 98 %): m.p. = 154–156 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.18$ (d, $J = 7.6$ Hz, 3 H), 7.66 (d, $J = 7.0$ Hz, 3 H), 7.32–7.13 (m, 4 H), 7.01 (t, $J = 7.4$ Hz, 3 H), 6.89 (d, $J = 14.7$ Hz, 3 H), 6.49 (d, $J = 6.5$ Hz, 3 H), 6.12 (s, 6 H), 5.53 ppm (d, $J = 14.7$ Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 142.51$, 142.21, 141.40, 141.01, 136.04, 132.64, 132.05, 127.37, 126.62, 125.14, 122.68, 121.68, 129.12, 114.45, 104.55, 52.07 ppm; FAB MS: m/z (%): 687 [M^+] (29), 307 (31), 154 (100); HR-MS (FAB): calcd for $C_{51}H_{34}N_3$: 688.2752; found: 688.2724.

Received: February 8, 2006

Keywords: charge transfer · cyclophanes · heterocycles · oxidation · radical ions

[1] a) F. Dierschkle, A. C. Grimsdale, K. Müllen, *Macromol. Chem. Phys.* **2004**, *205*, 1147–1154; b) Y. Takihana, M. Shiotsuki, F. Sanda, T. Masuda, *Macromolecules* **2004**, *37*, 7578–7583; c) K. Brunner, A. van Dijken, H. Börner, J. J. A. M. Bastiaansen, N. M. M. Kliggen, B. M. W. Langeveld, *J. Am. Chem. Soc.* **2004**, *126*, 6035–6042; d) H. Li, Y. Zhang, Y. Hu, L. Ma, X. Jing, F. Wang, *Macromol. Chem. Phys.* **2004**, *205*, 247–255; e) N. Drolet, J.-F. Morin, N. Leclerc, S. Wakin, Y. Tao, M. Leclerc, *Adv. Funct. Mater.* **2005**, *15*, 1671–1682.

[2] For a recent review, see: J. V. Grazulevivius, P. Strohriegl, J. Pielichowski, K. Pielichowski, *Prog. Polym. Sci.* **2003**, *28*, 1297–1353.

[3] a) N.-X. Hu, X. Shuang, Z. Popovic, B. Ong, A.-M. Hoor, *J. Am. Chem. Soc.* **1999**, *121*, 5097–5098; b) S. Wakim, J. Bouchard, M. Simard, N. Drolet, Y. Tao, M. Leclerc, *Chem. Mater.* **2004**, *16*, 4386–4388; c) Y. Wu, Y. Li, S. Gadner, B. S. Ong, *J. Am. Chem. Soc.* **2005**, *127*, 614–618; d) Y. Wu, Y. Li, S. Gadner, B. S. Ong, *Adv. Mater.* **2005**, *7*, 849–853.

[4] a) A. R. Mount, M. T. Robertson, *Phys. Chem. Chem. Phys.* **1999**, *1*, 5169–5177; b) P. Jennings, A. C. Jones, A. R. Mount, *Phys. Chem. Chem. Phys.* **2000**, *2*, 1241–1248; c) L. Greci, G. Tommasi, R. Petrucci, G. Marrosu, A. Trazza, P. Sgarabotto, L. Righi, A. Alberti, *J. Chem. Soc. Perkin Trans. 2* **2000**, 2337–2342.

[5] Compound **3** has been prepared by the acid-catalyzed reaction between indole and 3-bromoindole, which furnishes a complex mixture of indole dimers and trimers from which **3** can be obtained only in low yield: V. Bocchi, G. Palla, *Tetrahedron* **1986**, *42*, 5019–5024.

[6] J. M. Warman, P. M. de Haas, G. Dicker, F. C. Grozema, J. Piris, M. G. Debije, *Chem. Mater.* **2004**, *16*, 4600–4609.

[7] B. Gómez-Lor, A. M. Echavarren, *Org. Lett.* **2004**, *6*, 2993–2996.

[8] N. Robertson, S. Parsons, E. J. MacLean, R. A. Coxall, R. A. Mount, *J. Mater. Chem.* **2000**, *10*, 2043–2047.

[9] a) B. Speisser in *Modern Cyclophane Chemistry* (Eds: R. Gleiter, H. Hopf), Wiley-VCH, Weinheim, **2004**; b) G. B. Bartholemew, G. C. Bazan, *Acc. Chem. Res.* **2001**, *34*, 30–39.

[10] We have previously reported the synthesis of the all-carbon analogue: a) Ó. de Frutos, B. Gómez-Lor, T. Granier, M. A. Monge, E. Gutiérrez-Puebla, A. M. Echavarren, *Angew. Chem.* **1999**, *111*, 1552–1555; *Angew. Chem. Int. Ed.* **1999**, *38*, 205–207; b) Ó. de Frutos, B. Gómez-Lor, T. Granier, M. A. Monge, E. Gutiérrez-Puebla, A. M. Echavarren, *Chem. Eur. J.* **2002**, *8*, 2879–2890.

[11] a) V. M. Domingo, X. Burelons, E. Brillas, J. Carrilla, J. Rius, X. Torrelles, L. Juliá, *J. Org. Chem.* **2000**, *65*, 6847–6855; b) L. R. Milgrom, W. D. Flitter, *Tetrahedron* **1993**, *49*, 507–514; c) L. Eberson, F. Radner, *J. Chem. Soc. Chem. Commun.* **1991**, 1233–1234.

[12] A. Alberti, B. Ballarin, M. Guerra, D. Macciantelli, A. Mucci, F. Parenti, L. Schenetti, R. Seeber, C. Zanardi, *ChemPhysChem* **2003**, *4*, 1216–1225.

[13] a) R. Rathore, C. Zu, S. V. Lindeman, J. K. Kochi, *J. Chem. Soc. Perkin Trans. 2* **2000**, 1837–1840; b) L. Eberson, F. Radner, *Acta Chem. Scand.* **1998**, *52*, 114–130.

[14] Aromatic donor molecules tend to self-associate with their corresponding radical cations, thereby yielding dimeric electronically delocalized structures: a) J. K. Kochi, R. Rathore, P. Le Maguerés, *J. Org. Chem.* **2000**, *65*, 6826–6836, and references therein; b) D.-L. Sun, S. V. Rosokha, S. V. Lindeman, J. K. Kochi, *J. Am. Chem. Soc.* **2003**, *125*, 15950–15963; c) M. Yoshizawa, K. Kumazawa, M. Fujita, *J. Am. Chem. Soc.* **2005**, *127*, 13456–13457.

[15] The compound crystallizes in the triclinic system. Given that, in this system, the space group is not unequivocally determined through the systematic extinctions, the structure was solved in both the $P1$ and $P\bar{1}$ space groups. After careful analysis of the results in the acentric group, no significant geometrical differences were observed either in the independent cyclophane molecules or in the dimeric anion. Consequently, the structure presented here corresponds to that solved in the $P\bar{1}$ group: A. L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, **2005**.

[16] The shared hydrogen atom in the trifluoroacetate dimer has been observed in a Δ Fourier map in both the P1 and $P\bar{1}$ space groups.

[17] a) A. Kunze, R. Gleiter, F. Rominger, *Chem. Commun.* **1999**, 171–172; b) J. Pawlas, M. Kawatsura, J. F. Hartwig, *J. Am. Chem. Soc.* **2002**, *124*, 3669–3679.

[18] P. Le Maguerés, S. V. Lindeman, J. K. Kochi, *Org. Lett.* **2000**, *2*, 3567–3570.

[19] S. I. Hauck, K. V. Lakshimi, J. F. Hartwig, *Org. Lett.* **1999**, *1*, 2057–2060.

[20] a) See reference [14a]; b) P. Le Maguerés, S. V. Lindeman, J. K. Kochi, *J. Chem. Soc. Perkin Trans. 2* **2001**, 1180–1185; c) D. Sun, S. V. Rosokha, J. K. Kochi, *J. Am. Chem. Soc.* **2004**, *126*, 1388–1401.

[21] A. Ito, K. Tanaka, K. Kanemoto, T. Kato, *J. Org. Chem.* **2002**, *67*, 491–498. The same trends were observed for trifluoroacetic acid (slow) and $SbCl_5$ (fast). We refrained from using $SbCl_5$ due to the strong spectral overlap in the UV and Vis region.

[22] Software for the SMART system, V.5.04, Bruker-Siemens Analytical X-ray Instruments, Inc., Madison, WI, USA, **1998**.

[23] G. M. Sheldrick, SHELXL97, Program for Crystal Structure Refinement, University of Göttingen, Germany, **1997**.