possibility that the reactivity of **2** with respect to a diaryl(trifluoromethanesulfonyloxy)telluronium salt which could be initially formed is lower than that of **1**.

[10] Both reactions in the absence of O_2 in CH_3CN were monitored by ESR spectroscopy. However, no ESR signals were detected. Even if a radical cation is formed, its concentration would be quite low.

[11] Diphenyl sulfoxide reacts with Tf_2O to form a diphenyl(trifluoromethanesulfonyloxy)sulfonium salt: B. A. Garcia, J. L. Poole, D. Y. Gin, *J. Am. Chem. Soc.* **1997**, *119*, 7597–7598.

[12] For diaryltellurium bis(trifluoroacetate), see Y. Takaguchi, H. Fujihara, N. Furukawa, *J. Organomet. Chem.* **1995**, *498*, 49–52.

[13] Dimethyl sulfide reacts with Tf_2O to produce a dimethyl(trifluoromethanesulfonyl)sulfonium salt: V. G. Nenajdenko, P. V. Vertelezkij, A. B. Koldobskij, I. V. Alabugin, E. S. Balenkova, *J. Org. Chem.* **1997**, *62*, 2483–2486.

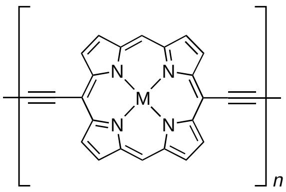
[14] Crystal structure analysis of **3b**: crystal dimensions $0.15 \times 0.25 \times 0.30$ mm, monoclinic, space group $P2_1/n$, $a = 13.318(4)$, $b = 18.319(7)$, $c = 14.871(4)$ Å, $\beta = 104.01(2)°$, $V = 3520(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.76$ g cm^{-3}, $2\theta_{max} = 51.9°$. Rigaku AFC-7R four-circle diffractometer, $Mo_{K\alpha}$ radiation, $\lambda = 0.71069$ Å, $\omega/2\theta$ scan mode, $T = 253$ K, 5330 measured reflections, Lorentzian and polarization corrections, absorption coefficient 18.5 cm^{-1}, semi-empirical absorption correction (Ψ scans; transmission factors 0.60–1.00), structure solution with direct methods (SIR92), package teXsan (1992), full-matrix least-squares refinement based on F, 2893 observed reflections ($I > 3.0\sigma(I)$), 424 parameters, hydrogen atoms included but not refined, $R = 0.036$, $R_w = 0.039$, residual electron density 0.51 e Å^{-3}. 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-100642. 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).

[15] For elements of Group 15 (E = Sb, Bi), insertion of O_2 molecules into E–E bonds occurs: a) F. Calderazzo, R. Poli, G. Pelizzi, *J. Chem. Soc. Dalton Trans.* **1984**, 2365–2369; b) H. J. Breunig, T. Krüger, E. Lork, *Angew. Chem.* **1997**, *109*, 654–655; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 615–617.

Enhanced Electronic Conjugation in Anthracene-Linked Porphyrins

Peter N. Taylor, Andrew P. Wylie, Juhani Huuskonen, and Harry L. Anderson*

Porphyrin polymers such as **1** (side chains omitted for clarity) exhibit exceptionally strong third-order nonlinear optical (NLO) behavior[1] because of their extensive electronic conjugation. This is potentially useful for fabricating electro-optic modulators for telecommunications. However even in **1** the NLO coefficient $\chi^{(3)}$ is not high enough for practical devices, so we are exploring routes to more conjugated porphyrin polymers. Müllen et al. have shown that the incorporation of 9,10-anthrylene units in conjugated polymers reduces the band-gap by reducing the energy difference between the aromatic and quinoidal resonance structures.[2] Thus the anthracene/porphyrin polymer **2** might be expected to be more conjugated than **1** because the anthrylene units stabilize the quinoidal/cumulenic resonance structure **3**. 9,10-Diethynylanthracene units are also interesting because of their intense fluorescence and potential electroluminescence; several conjugated polymers containing these units have been synthesized.[3] Here we demonstrate, using model oligomers, that 9,10-diethynylanthracene spacers enhance the conjugation between *meso*-linked porphyrins better than butadiyne, 1,4-diethynylbenzene or 1,4-diethynylthiophene bridges.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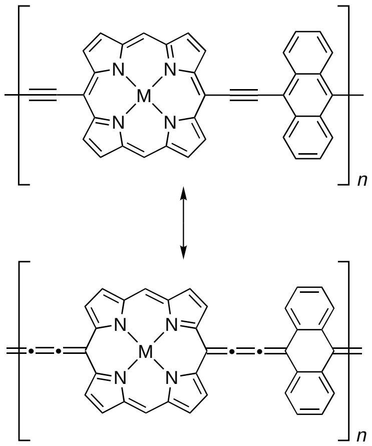
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There are numerous examples of molecules containing porphyrins and anthracenes linked either directly[4] or through saturated bridges,[5] polyenes,[6] and aromatic linkages.[7] Few of these exhibit much porphyrin–anthracene conjugation, because most unsaturated bridges twist out of plane with the porphyrin to avoid steric clashes. Alkynyl substituents are the only effective way of making conjugated connections to the *meso* position of a porphyrin. Marx and Breitmaier[8] have reported a porphyrin connected through alkynyl substituents to the 1-position of anthracene, but this does not allow resonance of the type postulated for **2** ↔ **3**.

To develop a synthetic route to conjugated anthracene/porphyrin oligomers we first synthesized **4** by the two routes shown in Scheme 1. Condensation of aldehyde **5**[9] with 3,5-

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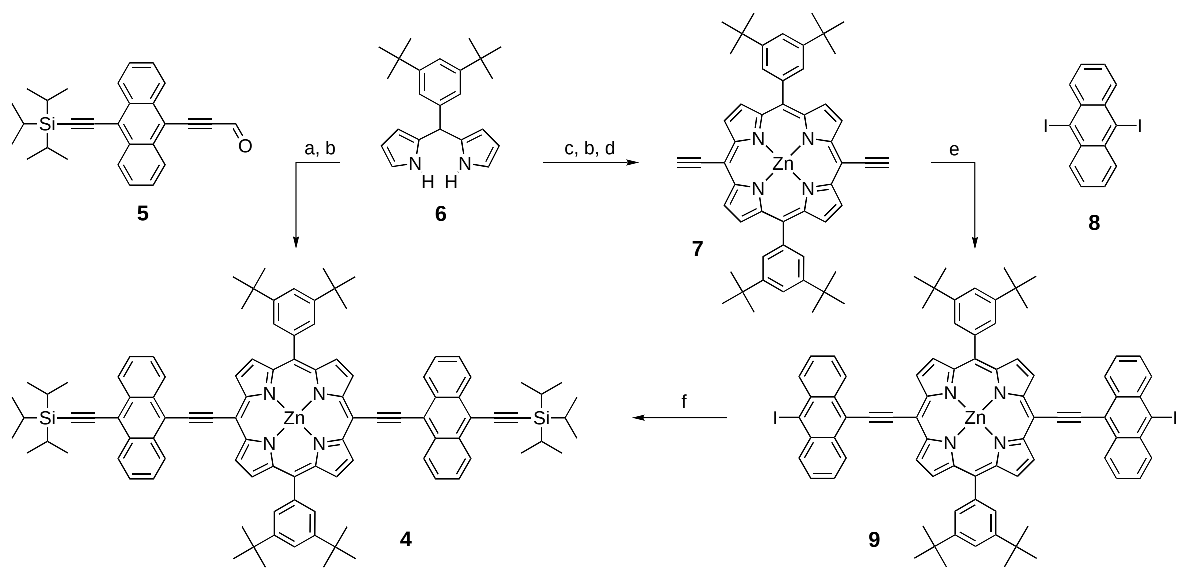


Scheme 1. a) **5**, $BF_3 \cdot OEt_2$, CH_2Cl_2 then 2,3-dichloro-5,6-dicyano-*para*-benzoquinone (DDQ), 9%; b) $Zn(OAc)_2$, 90%; c) Me_3SiC_2CHO, $BF_3 \cdot OEt_2$, CH_2Cl_2, then DDQ, 30%; d) Bu_4NF, CH_2Cl_2, 95%; e) $LiN(SiMe_3)_2$, THF then $ZnCl_2$ then **8**, $[Pd_2(dba)_3]$ (dba = 1,3-dibenzylideneacetone), $AsPh_3$, 13%; f) $i\text{Pr}_3SiC_2ZnCl$, $[Pd_2(dba)_3]$, $AsPh_3$, 39%.

di(*tert*-butylphenyl)dipyrromethane (**6**)[10] and subsequent oxidation and metalation gave **4** (8% yield from **6**). Short reaction times (3 mins) are needed to avoid forming mixtures of porphyrins because the porphyrinogen intermediate is prone to acid-catalyzed scrambling. In the second route, **4** is produced by palladium-catalyzed coupling. The 5,15-diethynylporphyrin **7** (prepared in 26% yield from **6** using established methodology[10]) was treated with excess 9,10-diiodoanthracene (**8**)[11] under modified Heck conditions to give **9**, which was coupled to triisopropylsilylacetylene under similar conditions to give **4** (5% overall yield from **7**).

The UV/Vis absorption spectrum of **4** is compared to those of reference compounds **10** and **11** in Figure 1. In contrast to other anthracene-containing porphyrin dyads the absorption spectrum of **4** is very different from those of both its components. The anthracene S_0-S_3 transition at 264 nm is abnormally weak in **4**, whereas the porphyrin S_0-S_2 B band (Soret) and S_0-S_1 Q band are unusually intense, as shown by oscillator strengths[12] f_B and f_Q in Table 1. The general increase in oscillator strength can be attributed to the extension of the porphyrin chromophore, while the intensification of the Q band is probably due to reduced a_{1u}-a_{2u} degeneracy.[1] Excitation of **4** at both 264 and 496 nm produces emission at 710 nm and there is close agreement between the excitation and absorption spectra showing that anthracene-to-porphyrin energy transfer is quantitative.

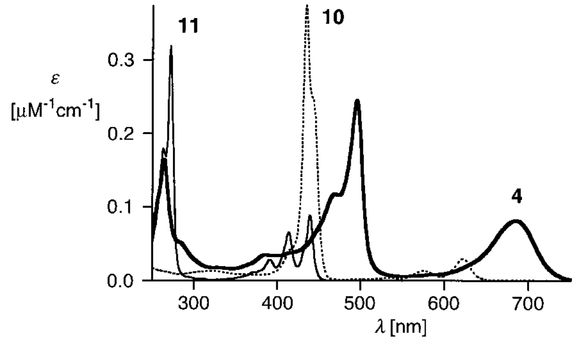
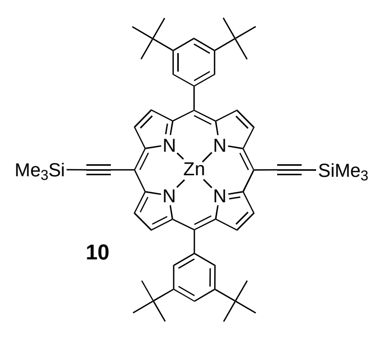


Figure 1. Absorption spectra of **4** (bold), **10** (dashed) and **11** (plain) in CH_2Cl_2. The spectrum of **11** is scaled up by a factor of 2 for better comparison with **4**.



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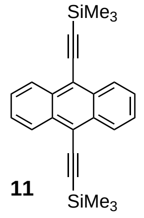

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Table 1. Summary of electronic spectra.[a]

Porphyrin	λ_B [nm]	λ_Q [nm]	λ_f [nm]	Φ_f	f_B	f_Q
10	436	578, 625	629	0.025	1.2	0.12
4	469, 496	685	710	0.048	1.9	0.40
13	441, 531	706	764	0.052	1.2	0.35
14	458, 494	675, 741	749	0.055	1.2	0.23
15	455	686	693	0.043	1.4	0.25
16	456, 496	704	719	0.053	1.4	0.23

[a] All spectra were recorded in 1% C_5H_5N/CH_2Cl_2, except those of **4** and **10** which are in CH_2Cl_2. λ_B and λ_Q are the absorption λ_{max}, and f_B and f_Q are the oscillator strengths[12] per porphyrin, for the B and Q bands; Φ_f is the fluorescence quantum yield.[13]

The crystal structure[14] of $\mathbf{4} \cdot 2\,(C_5H_5N)$ is shown in Figure 2. The bond lengths are normal[15] and show no manifestations of the distorted electronic structures of the porphyrin and anthracene chromophores. Interestingly, the plane of the anthracene units is at an angle of 40.90(7)° to that of the porphyrin. Molecular mechanics calculations indicate that

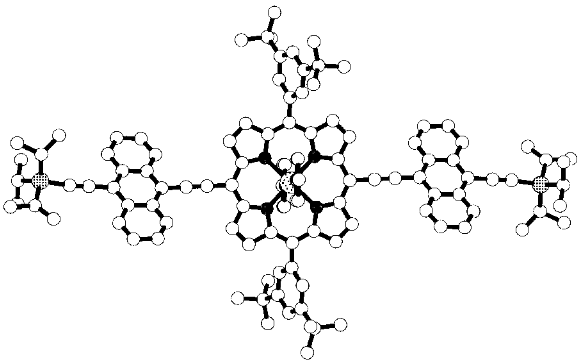
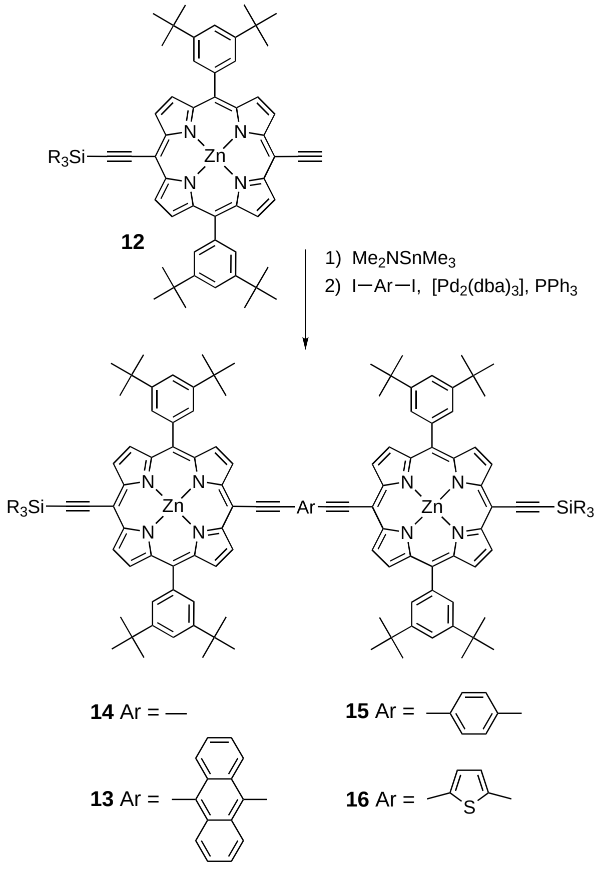


Figure 2. Crystal structure of porphyrin **4** · $(C_5H_5N)_2$.

there is no steric barrier to planarity, so the conformation is probably influenced by crystal packing.

Conjugated porphyrin dimers were synthesized as shown in Scheme 2. The terminal acetylene **12**[9] was stannylated, then Stille coupled with **8** to give the anthracene-linked dimer **13** in 46% yield and a small amount (ca. 5%) of the butadiyne-linked dimer **14**, which was also prepared by oxidative coupling of the terminal acetylene.[9] Similar conditions were used to prepare the 1,4-phenylene- and 2,5-thienylene-linked dimers **15** and **16** in 61 and 52% yield, respectively. Similar butadiyne-, benzene- and thiophene-linked dimers have been reported previously.[16] Selected spectroscopic data for **13**–**16** are listed in Tables 1 and 2.



Scheme 2. Synthesis of porphyrin dimers (R = *n*-hexyl).

Table 2. Selected spectroscopic data for porphyrin dimers **13**, **14**, and **15**.[a]

13: ^{1}H NMR: $\delta = 10.06$ (d, $J = 5$ Hz, 4H), 9.68 (d, $J = 5$ Hz, 4H), 9.52 (dd, $J = 7$ and 3 Hz, 4H), 9.02 (d, $J = 5$ Hz, 4H), 8.89 (d, $J = 5$ Hz, 4H), 8.08 (d, $J = 2$ Hz, 8H), 7.94 (dd, $J = 7$ and 3 Hz, 4H), 7.86 (t, $J = 2$ Hz, 4H), 1.82 (m, 12 H), 1.60 (s, 72H), 1.58 (m, 12H), 1.43 (m, 24H), 1.08 (m, 12H), 0.92 (t, $J = 7$ Hz, 18H); ^{13}C NMR: $\delta = 152.76$, 152.34, 150.96, 150.70, 148.92, 142.20, 133.59, 133.29, 132.93, 131.15, 130.84, 129.89, 128.43, 127.39, 124.56, 121.17, 120.03, 110.05, 107.64, 101.47, 101.27, 99.87, 94.44, 35.31, 33.54, 32.03, 31.94, 24.66, 22.87, 14.37, 14.27; IR (KBr): $\tilde{\nu}_{max} = 2135$ cm^{-1}; UV/Vis: $\lambda_{max}(\log\varepsilon) =$ 706 (4.96), 531 (4.91), 441 nm (5.18); TOF LD-MS: $m/z = 2335.1$ [M+H$^+$], correct for $C_{154}H_{186}N_8Si_2Zn_2$.

14: ^{1}H NMR: $\delta = 9.90$ (d, $J = 5$ Hz, 4H), 9.67 (d, $J = 5$ Hz, 4 H), 8.99 (d, $J =$ 5 Hz, 4H), 8.89 (d, $J = 5$ Hz, 4H), 8.06 (d, $J = 2$ Hz, 8H), 7.83 (t, $J = 2$ Hz, 4H), 1.79 (m, 12 H), 1.58 (s, 72H), 1.56 (m, 12H), 1.40 (m, 24H), 1.04 (m, 12H), 0.91 (t, $J = 7$ Hz, 18H); ^{13}C NMR: $\delta = 153.11$, 152.37, 150.89, 150.44, 148.76, 141.89, 133.37, 132.88, 131.09, 130.73, 130.11, 124.55, 121.04, 109.78, 101.73, 99.83, 99.46, 88.83, 82.56, 35.25, 33.57, 31.98, 31.90, 24.60, 22.89, 14.37, 14.14; IR (KBr): $\tilde{\nu}_{max} = 2135$ cm^{-1}; UV/Vis: $\lambda_{max}(\log\varepsilon) = 741$ (5.11), 675 (4.91), 494 (5.34), 458 nm (5.62); TOF LD-MS: $m/z = 2159.3$ [M+H$^+$], correct for $C_{140}H_{178}N_8Si_2Zn_2$.

15: ^{1}H NMR: $\delta = 9.81$ (d, $J = 5$ Hz, 4H), 9.68 (d, $J = 5$ Hz, 4H), 8.96 (d, $J =$ 5 Hz, 4H), 8.89 (d, $J = 5$ Hz, 4H), 8.20 (s, 4H), 8.07 (d, $J = 2$ Hz, 8H), 7.86 (t, $J = 2$ Hz, 4H), 1.83 (m, 12H), 1.61 (s, 72H), 1.59 (m, 12H), 1.44 (m, 24H), 1.06 (m, 12H), 0.93 (t, $J = 7$ Hz, 18H); ^{13}C NMR: $\delta = 152.50$, 152.02, 150.73, 150.57, 148.75, 141.99, 133.04, 132.92, 131.91, 131.03, 130.63, 130.12, 124.40, 124.30, 121.01, 109.88, 101.14, 100.64, 99.55, 96.56, 96.29, 35.27, 33.59, 32.01, 31.92, 24.62, 22.90, 14.39, 14.18; IR (KBr): $\tilde{\nu}_{max} = 2137$ cm^{-1}; UV/Vis: $\lambda_{max}(\log\varepsilon) = 686$ (5.18), 455 nm (5.65); TOF LD-MS: $m/z = 2235.1$ [M+H$^+$], correct for $C_{146}H_{182}N_8Si_2Zn_2$.

[a] ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra were recorded in 1% $C_5D_5N/CDCl_3$ and UV/Vis spectra in 1% C_5H_5N/CH_2Cl_2.

The absorption and emission spectra of three of the dimers, **13**, **14**, and **15** are shown in Figures 3 and 4. The effect of the anthracene unit on porphyrin–porphyrin electronic coupling is best seen by comparing the emission spectra of **13** and **15**. The distance between the porphyrins is the same in these two dimers, yet the emission from **13** is red-shifted by 71 nm

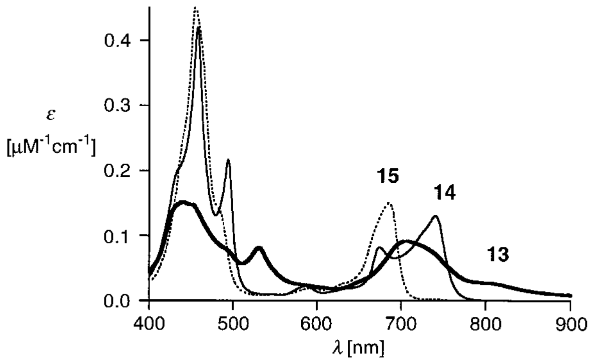


Figure 3. Absorption spectra of dimers **13** (bold), **14** (plain), and **15** (dashed) in 1% C_5H_5N/CH_2Cl_2.

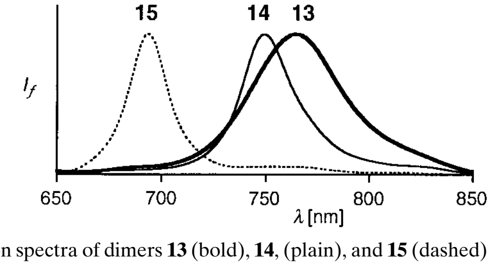


Figure 4. Emission spectra of dimers **13** (bold), **14**, (plain), and **15** (dashed) in 1% C_5H_5N/CH_2Cl_2.

indicating strong porphyrin–porphyrin conjugation. Comparing **13**, **15** and **16** shows that the thiophene unit leads to more conjugation than phenylene, but less than anthracene. It is remarkable that the 9,10-diethynylanthracene bridge allows even more electronic communication than the simple butadiyne link in **14**. This implies that longer oligomers of type **2**/**3** should have strong third-order NLO behavior.

Experimental Section

13: A solution of **12**[9] (54 mg, 50 µmol) in THF (8 mL) and pyridine (80 µL) was treated with dimethylaminotrimethyltin (41 µL, 250 µmol) at 50 °C for 2 h, then evaporated. To the resulting waxy residue was added THF (8 mL), **8**[11] (11 mg, 25 µmol), tris(dibenzylideneacetone)dipalladium(0) (2.7 mg, 3 µmol), and triphenylphosphane (3.1 mg, 12 µmol) under argon. The mixture was stirred at 50 °C for 24 h. Purification by chromatography on silica (eluting with 50/2/1 petroleum ether (60–80 °C)/ethyl acetate/pyridine) and recrystallization from CH_2Cl_2/methanol yielded **13** as a brown solid (27 mg, 46 %).

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[9] The synthesis of **5**, **12,** and **14** will be detailed elsewhere.

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[14] Crystals were grown by slow diffusion of n-pentane into a solution of **4** in 1 % $C_5H_5N/CHCl_3$, over two weeks. Crystal structure analysis for **4** · 2 C_5H_5N: $M_r = 1667.66$, triclinic, space group $P\bar{1}$, $a = 11.052(2)$, $b = 13.110(2)$, $c = 16.970(4)$ Å, $\alpha = 81.88(2)$, $\beta = 89.68(2)$, $\gamma = 77.20(2)°$, $V = 2372.9(8)$ Å^3, $Z = 1$, $T = 293$; $\rho_{calc} = 1.167$ g cm^{-3}; $\mu = 0.987$ mm^{-1}, crystal dimensions 0.25 × 0.35 × 0.45 mm; diffractometer: Enraf-Nonius MACH3; radiation $Cu_{K\alpha}$ ($\lambda = 1.54184$ Å); scan mode: $\omega/2\theta$; range: $3.5 < \theta < 74.6$; measured reflections: 10156; independent reflections: 9712 ($R_{int} = 0.0186$); corrections applied: Lorentz polarization and experimental absorption correction (psi-scans, A. C. T. North, D. C. Phillips, F. S. Mathews, *Acta Crystallogr. A* **1968**, *24*, 351–359) T_{min}/T_{max} 0.7302/0.7839; R values ($I > 2\sigma I$): $R1 = 0.0847$, $wR2 = 0.2492$, all data: $R1 = 0.1344$, $wR2 = 0.2784$. Structure solution with direct methods (SHELXS-86, G. Sheldrick, 1990). Structure refinement (SHELXL-93, G. Sheldrick, 1993): Full-matrix least squares methods against F^2; 548 parameters, 28 constraints, max/min residual electron density 0.662/−0.825 e Å^{-3}. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated positions. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-100671. 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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The Azide-Nitrilimine Analogy in Aluminum Chemistry[**]

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Covalent azides of type **A** are well-known 1,3-dipoles that have found widespread application in organic synthesis,[1] and that are also of increasing importance in inorganic chemistry.[2] Aluminum azides possess a rich structural diversity (derivatives **C**–**G**[3]) and constitute valuable single-source

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