Available online at www.sciencedirect.com

Tetrahedron Letters 45 (2004) 329–333

Tetrahedron Letters

Preparation, properties, and X-ray structures of 5,5′-bi(8-aminoquinoxalyl)s: novel Wurster-type electron donors with a heterobiaryl skeleton

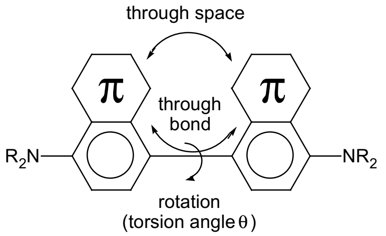
Takanori Suzuki,* Mayu Saito, Hidetoshi Kawai, Kenshu Fujiwara and Takashi Tsuji

Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan

Received 6 October 2003; revised 24 October 2003; accepted 27 October 2003

Abstract—The title electron donors were prepared by the double condensation reactions of 2,2′,3,3′-tetraamino-4,4′-bis(1-pyrrolidinyl)biphenyl with 1,2-diketones. They adopt twisted conformations in crystal, yet the reversible two-stage one-electron oxidation process suggests the planar geometries for the oxidized species. Depending on the nature of substituents on the pyrazine ring, this π-system can be endowed additional features such as chiroptical properties or metal coordination ability.

1,4-Phenylenediamines and benzidines (4,4′-diaminobiphenyls) have been known as the representative Wurster-type redox systems.[1] The former derivatives possess stronger electron-donating properties and higher stability in the oxidized form,[2] and thus have been used as versatile building blocks in developing functionalized materials such as electroluminescent devices[3] or nonlinear optical materials.[4] In contrast, studies on the latter are less explored although benzidine is a promising π-system in constructing hole-transport materials[5] or bis(azomethine)-type pigments.[6]



Scheme 1.

From the viewpoint of switching phenomenon of organic redox systems,[7] the benzidine skeleton is more attractive since the external stimuli such as electric potentials may alter the torsion angle of the biaryl moiety,[8] which in turn affects the physical properties of the whole molecule by modifying the through-bond and/or through-space interaction between the molecular halves (Scheme 1): the through-bond interaction will be maximized in the planar conformation ($\theta = 0°$ or $180°$) whereas the through-space interaction will be more effective with the small torsion angle around the biaryl axis ($\theta \leqslant 90°$). With these in mind, the title diamines **1** with a scarcely examined 5,5′-biquinoxalyl skeleton[9] were designed as a new class of Wurster-type electron donors that may undergo two-stage one-electron oxidation as shown in Scheme 2.

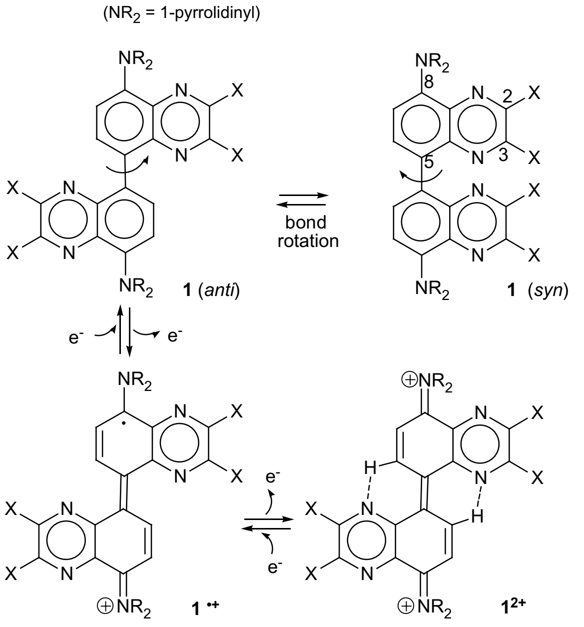
It is likely that the twisted structure, either *syn* ($\theta < 90°$) or *anti* ($\theta > 90°$), is preferred for the neutral **1** due to the repulsive interaction between the annelated pyrazine rings. In contrast, the oxidized forms ($\mathbf{1}^{+\cdot}$ and $\mathbf{1}^{2+}$) may adopt the planar conformation to realize spin and/or charge delocalization over the whole π-system. Increased acidity of C(sp^2)–H protons in the oxidized form also favors the *anti*-planar conformation ($\theta = 180°$) in terms of the intramolecular C–H···N-type hydrogen bonds.[12] 1-Pyrrolidinyl group but not Me$_2$N or H$_2$N was chosen as the amino substituents on the biaryl skeleton in order to assure strong electron-donating properties for **1**.[13] Here we report their preparation and redox properties as well as the detailed

---

Keywords: electron donor; benzidine; biquinoxalyl; biaryl; redox system; through-bond interaction; through-space interaction; metal coordination.

* Corresponding author. Tel.: +81-11-706-2714; fax: +81-11-706-2714; e-mail: tak@sci.hokudai.ac.jp

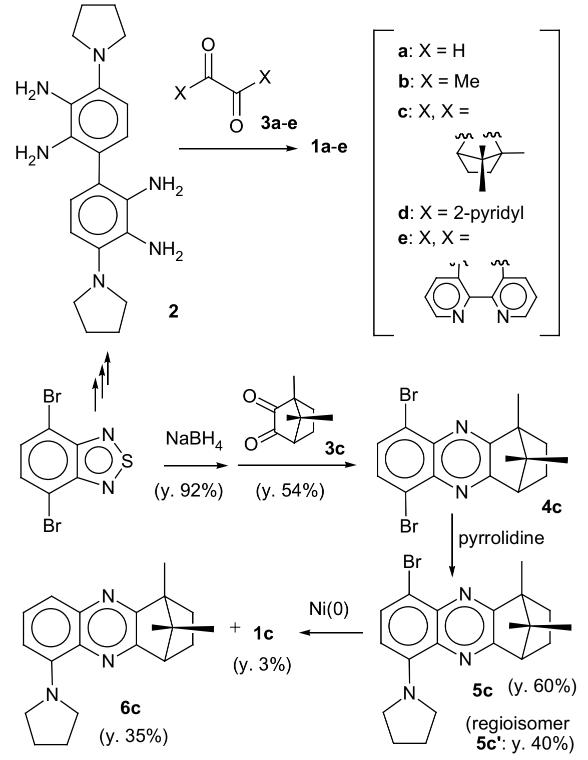
0040-4039/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2003.10.151



Scheme 2.

molecular geometries determined by low-temperature X-ray analyses. It is noteworthy that the additional features, such as chiroptical properties or metal coordination ability, can be endowed by the substituents on the annelated pyrazine ring in **1**.

2,2′,3,3′-Tetraamino-4,4′-bis(1-pyrrolidinyl)biphenyl **2**[8a] was prepared from 4,7-dibromobenzothiadiazole[14] in three steps and used as the common starting material in this study. Condensation of this hexamine with glyoxal **3a** (as 1,4-dioxane-2,3-diol) in AcOH or diacetyl **3b** in EtOH gave yellow and orange crystals of **1a** and **1b** in 4% and 41% yield, respectively (Scheme 3). A similar reaction of **2** with (*1R*)-(−)-camphorquinone **3c** is expected to produce three isomers, in which the quaternary methyl groups of chiral auxiliaries are directed inward–inward, inward–outward, and outward–outward, respectively. Experimentally the double condensation in EtOH gave the inward–inward isomer **1c** as a major product in 37% isolated yield. Although the reason for the preferred formation of **1c** over the other two is not clear at this moment, its structure could be deduced by the independent preparation through Ni(0)-catalyzed homo-coupling[15] of the bromo-substituted molecular half **5c** (Scheme 3)[16] and finally confirmed by the X-ray analysis[17] (Fig. 1). Reactions of **2** with 2,2′-pyridil (**3d**) and 1,10-phenanthroline-5,6-dione (**3e**) proceeded smoothly in EtOH to give red and violet crystals of **1d** and **1e** in 55% and 25% yield, respectively.



Scheme 3.

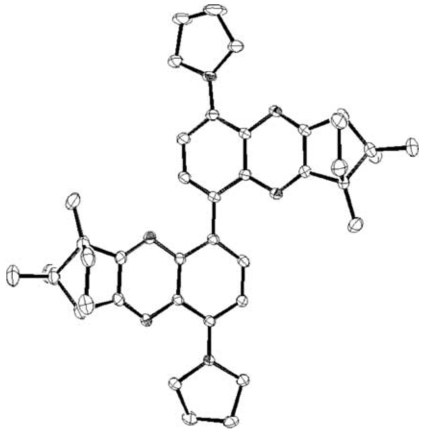


Figure 1. Molecular structure of **1c** determined by X-ray analysis at 153 K.

X-ray analysis showed that the tetrakis(2-pyridyl) derivative **1d** adopts *syn*-conformation in crystal ($\theta = 44.5°$, Fig. 2),[17] which is in contrast to **1c** with the *anti*-geometry ($\theta = 133.3°$). These results are indicative of the rotational freedom of the π-framework in **1**. Since no special interaction seems at work between the pyridyl substituents in **1d**, preference of *syn* or *anti* conformation in the solid state may be largely affected by crystal packing force but not by intramolecular interactions. It is noteworthy that both of **1c** and **1d** are much more flattened than the solid-state structure of parent 5,5′-biquinoxalyl **7**[9] without amino substituents ($\theta = 74.1°$)[18] analyzed in this study.[17] Detailed comparisons of bond lengths showed that the values of **1c** and **1d** are close to each other whereas they differ significantly from those of **7**. As highlighted by underlines in Table 1, huge differences (0.024–0.045 Å) are observed in the benzidine moiety (bonds c, d, d′, g, and i). Thus, bonds c, d, and d′ are longer in **1** than **7** whereas bonds g and i exhibit the reverse order. Such differences can be best described by considering the contributions from the polarized structures **A** and **B** shown in Scheme 4, which is consonant

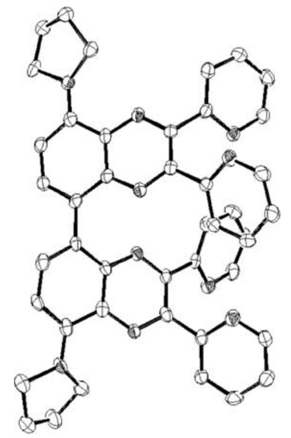
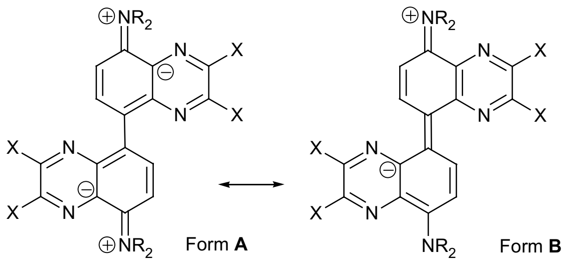
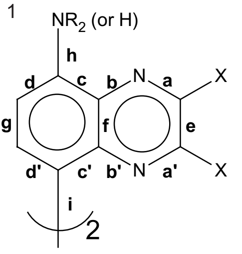


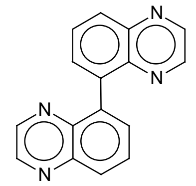
Figure 2. Molecular structure of **1d** determined by X-ray analysis at 153 K.



Scheme 4.

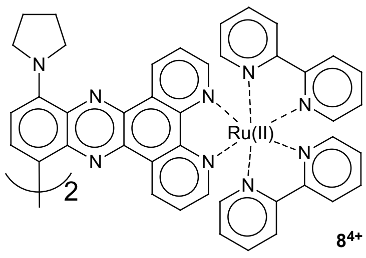
Formula 1





7

Formula 2



8^{4+}

with the shorter C_{Ar}–NR_2 bonds in **1** (bond h) than the typical values (1.39–1.41 Å).[20] The form **B** postulates the through-bond interaction between two molecular halves over the central biaryl bond, and increased π-bond order of bond i can account for the less twisted conformation in **1** than in **7**. Since the polarized forms are stabilized by electron-withdrawing groups on the pyrazine ring, **1d** exhibit huge differences more often than **1c** due to much contributions from **A** and **B**.

Bi(8-aminoquinoxalyl)s inherit the intrinsic redox properties from benzidine, and **1a**–**d** undergo reversible two-stage one-electron oxidation (Table 2) despite the twisted geometry for the neutral species. Slightly negative values of E_1^{ox} in **1b** and **1c** than others are due to the electron-donating alkyl substituents on the pyrazine ring. Electron-donating properties of **1** are similar to that of *N*,*N*,*N'*,*N'*-tetramethylbenzidine (TMB; E_1^{ox} = +0.49 V; E_2^{ox} = +0.76 V; ΔE = 0.27 V; measured under the similar conditions to Table 2), and noteworthy is the similar ΔE for TMB and **1** (0.16–0.21 V). Since the value of ΔE is quite sensitive to the molecular planarity of

Table 1. Listing of bond lengths (Å) in **1c**,[a] **1d**,[a] and **7** determined by X-ray analyses at 153 K[b]

Compound	a	a'	b	b'	c	c'	d	d'	e	f	g	h	i
1c	1.298	1.298	1.386	1.386	1.436	1.426	1.393	1.377	1.427	1.438	1.397	1.378	1.489
1d	1.328	1.320	1.365	1.376	1.449	1.426	1.402	1.398	1.419	1.429	1.386	1.362	1.479
7	1.314	1.305	1.370	1.370	1.413	1.419	1.357	1.368	1.419	1.421	1.414	—	1.503

[a] Averaged over the assumed C_2 symmetry.

[b] Estimated standard deviations are 0.003–0.005, 0.006–0.007, and 0.004–0.005 Å in **1c**, **1d**, and **7**, respectively.

Table 2. Redox potentials and spectral properties of new donors **1**

Compound		E_1^{ox} (V)[a]	E_2^{ox} (V)[a]	ΔE (V)[b]	λ_{max} (nm) (log ε)[c]	λ_{em} (nm)[d]
1a	(X = H)	+0.48	+0.64	0.16	449 (3.71), 279 (4.49)	530
1b	(X = Me)	+0.37	+0.54	0.17	424 (3.94), 280 (4.88)	546
1c	(X–X: bornene)	+0.35	+0.53	0.18	411 (4.12), 284 (4.94)	541
1d	(X = 2-pyridyl)	+0.47	+0.68	0.21	477 (4.13), 301 (4.89), 257 (4.74)	596[f]
1e	(X–X: phenanthroline)	+0.43[e]	+0.63[e]	0.20[e]	547 (3.67), 341 (4.61), 258 (4.75)	—[g]

[a] Redox potentials were measured in CH_2Cl_2 containing 0.1 mol dm^{-3} nBu$_4$NPF$_6$ and are reported in V versus SCE (scan rate 100 mV s^{-1}).

[b] $\Delta E = E_2^{ox} - E_1^{ox}$.

[c] UV–vis spectra were measured in CH_2Cl_2.

[d] Fluorescence spectra were measured in CH_2Cl_2.

[e] Due to the low solubility of **1e**, the peaks in voltammogram are ambiguous.

[f] Weak.

[g] Very weak.

cation–radical species,[21] the similarity in ΔE suggests the planar structure for $\mathbf{1}^{+\cdot}$ as in the case of TMB. This is the indication of the redox-assisted control of the biaryl torsion angle in **1** although confirmation by the structural analysis on the oxidized form has been still unsuccessful due to the difficulty in obtaining the pure salt of $\mathbf{1}^{+\cdot}$ and/or $\mathbf{1}^{2+}$.

Newly prepared donors **1a–e** are stable colorful crystals, and all of them show broad absorptions in the visible region (Table 2). They are assigned to the intramolecular charge-transfer (CT)-type absorptions from the HOMO mainly localized on the benzidine unit to the LUMO and/or NLUMO that has large coefficients in pyrazine units. This idea is supported by the red-shifted absorption maximum in **1d** and **1e** with low-lying vacant orbitals due to the electron-withdrawing nitrogen heterocycles attached on the pyrazine ring. Compounds **1a–c** emit green fluorescence, and its apparent intensity is weakened in **1d**. Phenanthroline derivative **1e** is nearly nonfluorescent. These results are in accord with the increased intramolecular CT nature[22] of the excited state in **1d** and **1e**.

Besides the general features of **1** described above, the substituents on the pyrazine ring can endow this π-skeleton with additional properties. For example, the chiral auxiliaries in **1c** lead the axial chirality to be (*S*) for all molecules in crystal (Fig. 1). The CD spectra of solid-state sample (KBr disk) and CH_2Cl_2 solution are similar with a characteristic negative couplet centered 270 nm. This result indicates that the major conformer of **1c** in solution may also adopt (*S*)-configuration about the biaryl axis. In this way, the distal asymmetric centers can control the chiroptical properties of the biaryl framework. Although the mol CDs ($\Delta\varepsilon$) in **1c** are not spectacular (−24.2 at 278 nm, +10.1 at 259 nm in CH_2Cl_2), the couplet in the spectrum clearly shows the through-space exciton-type interaction between the molecular halves since the molecular half **6c** only exhibits positive Cotton effect ($\Delta\varepsilon + 15.6$ at 286 nm) but not couplet. Another interesting feature is the metal coordination ability[23] of the pyridine containing derivatives **1d** and **1e**. Preliminary studies show that **1e** acts as a ditopic ligand at the two phenanthroline units. Thus, the complexation of **1e** with Ru(2,2′-bipyridyl)$_2$Cl$_2$ proceeded smoothly to give the complex $\mathbf{8}^{4+}(PF_6^-)_4$ as a green powder in 92% yield, whose structure was deduced by ^1H NMR and ESI–MS spectra and elemental analysis.[24] Studies on the intramolecular interaction between two metal centers in $\mathbf{8}^{4+}$ as well as further examinations on metal complexation of **1d** and **1e** are now under way.

In summary, we have succeeded in developing a new class of heterobiaryl-type electron donors **1** with a rotational freedom. X-ray analyses on neutral donors **1c** and **1d** indicate the through-bond interaction across the biaryl axis whereas the through-space interaction caused the exciton-type chiroptical activity in **1c**; both interactions would be modified as a function of the torsion angle around the biaryl axis. This study has provided a unique prototype for further examinations of switching phenomenon of organic redox systems by controlling the torsion angle[25] upon input of external stimuli.

Supplementary material

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 218192-218194. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 (0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

This work was supported by the Ministry of Education, Culture, Sports, Science and Technology, Japan (No. 15350019 and 14654139). We are grateful to Dr. Yoshiaki Tsubata (Sumitomo Chemical Co.) for his helpful discussion. We thank Prof. Tamotsu Inabe (Hokkaido University) for use of the X-ray structure analysis system. MS spectra were measured by Dr. Eri Fukushi and Mr. Kenji Watanabe at the GC-MS and NMR Laboratory (Faculty of Agriculture, Hokkaido University).

References and Notes

1. Deuchert, K.; Hünig, S. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 875.
2. Nelsen, S. F.; Tran, H. Q.; Nagy, M. A. *J. Am. Chem. Soc.* **1998**, *120*, 298.
3. (a) Li, H.; Hu, Y.; Zhang, Y.; Ma, D.; Wang, L.; Jing, X.; Wang, F. *Chem. Mat.* **2002**, *14*, 4484; (b) Okamoto, T.; Terada, E.; Kozaki, M.; Uchida, M.; Kikukawa, S.; Okada, K. *Org. Lett.* **2003**, *5*, 373.
4. (a) Asselberghs, I.; Zhao, Y.; Clays, K.; Persoons, A.; Comito, A.; Rubin, Y. *Chem. Phys. Lett.* **2002**, *364*, 279; (b) Suzuki, T.; Tsuji, T.; Okubo, T.; Okada, A.; Obana, Y.; Fukushima, T.; Miyashi, T.; Yamashita, Y. *J. Org. Chem.* **2001**, *66*, 8954.
5. (a) Schumann, J.; Kanitz, A.; Hartmann, H. *Synthesis* **2002**, 1268; (b) Sakanoue, K.; Motoda, M.; Sugimoto, M.; Sakaki, S. *MCLC S&T, Sect. B: Nonlinear Opt.* **2000**, *26*, 271.
6. (a) Hinks, D.; Freeman, H. S.; Arai, Y.; Ando, H. *Dyes Pigments* **2001**, *48*, 7; (b) Sokolowska, J.; Hinks, D.; Freeman, H. S. *Dyes Pigments* **2001**, *48*, 15.
7. (a) Raymo, F. M.; Stoddart, J. F. In *Molecular Switches*; Feringa, B. L., Ed.; Wiley-VCH, 2001; p 219; (b) Colasson, B. X.; Dietrich-Buchecker, C.; Jimenez-Melero, M. C.; Sauvage, J.-P. *J. Phys. Org. Chem.* p 476; (c) Suzuki, T.; Higuchi, H.; Tsuji, T.; Nishida, J.; Yamashita, Y.; Miyashi, T. In *Chemistry of Nanomolecular System, Chapter 1: Dynamic Redox Systems*; Nakamura, T., Matsumoto, T., Tada, H., Sugiura, K., Eds.; Springer: Berlin, 2003; p 3.
8. (a) Suzuki, T.; Okubo, T.; Okada, A.; Yamashita, Y.; Miyashi, T. *Heterocycles* **1993**, *35*, 395; (b) Higuchi, H.; Ohta, E.; Kawai, H.; Fujiwara, K.; Tsuji, T.; Suzuki, T. *J. Org. Chem.* **2003**, *68*, 6605.

9. Only a limited number of 5,5′-biquinoxalyl derivatives are known to date, namely, the parent molecule **7** (Ref. 10), and 2,2′,3,3′-tetraphenyl or 2,2′,3,3′-tetrakis(4-methylphenyl) derivatives (Ref. 11). According to the CCDC database, none of them has been analyzed crystallographically, so that, there is no experimental information on the geometrical feature of this skeleton.
10. (a) Tsubata, Y. Dissertation, Faculty of Science, Tohoku University, 1992; (b) Miyamoto, E.; Imanaka, Y. *Jpn. Kokai Tokkyo Koho*, JP93-298677; *Chem. Abst.* **1995**, *123*, 213140.
11. Nakamura, H.; Hironaka, Y.; Kusumoto, T. *Jpn. Kokai Tokkyo Koho*, JP93-173402; *Chem. Abst.* **1995**, *122*, 277722.
12. (a) Taylor, R.; Kennard, O. *J. Am. Chem. Soc.* **1982**, *104*, 5063; (b) Cotton, F. A.; Daniels, L. M.; Jordan, G. T., IV, Murillo, C. A. *Chem. Commun.* **1997**, 1673; (c) Steiner, T.; Desiraju, G. R. *Chem. Commun.* **1998**, 891; (d) Fukushima, T.; Okazeri, N.; Miyashi, T.; Suzuki, K.; Yamashita, Y.; Suzuki, T. *Tetrahedron Lett.* **1999**, *40*, 1175; (e) Ohkita, M.; Suzuki, T.; Nakatani, K.; Tsuji, T. *Chem. Lett.* **2001**, 988.
13. 1,4-Bis(1-pyrrolidinyl)benzene ($E^{\text{ox}} = -0.02$ V vs SCE in MeCN) exhibits much stronger donating properties than *N,N,N′,N′*-tetramethyl-1,4-phenylenediamine (+0.10 V) (Ref. 4b). Preliminary study showed that 5,5′-bi-(8-dimethylaminoquinoxalyl)**1a′** ($NR_2 = NMe_2$, X = H), which was obtained by the condensation reaction of 2,2′,3,3′-tetraamino-4,4′-bis(dimethylamino)biphenyl,[8a] and glyoxal, exhibits only moderate donating properties (+0.61 V). Under the similar conditions, E^{ox} of **1a** is much less positive (+0.50 V) than **1a′**.
14. Pilgram, K.; Zupan, M.; Skiles, R. *J. Heterocycl. Chem.* **1970**, *7*, 629.
15. Iyoda, M.; Otsuka, H.; Sato, K.; Nisato, N.; Oda, M. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 80.
16. This route is suitable to obtain the inward–inward isomer **1c** without concomitant formation of other two isomers, yet the final homo-coupling reaction of **5c** was unreproducible and also inefficient due to the by-production of **6c**. Attempted homo-coupling of **5c′** into the outward–outward isomer of **1c** has been still unsuccessful.
17. Crystal data of **1c**: $C_{40}H_{48}N_6$, M 612.86, monoclinic, $P21$, $a = 12.257(5)\,\text{Å}$, $b = 7.780(3)\,\text{Å}$, $c = 17.838(7)\,\text{Å}$, $\beta = 98.273(6)°$, $U = 1683(1)\,\text{Å}^3$, $D_c\ (Z = 2) = 1.209\,\text{g cm}^{-1}$, $\mu = 0.72\,\text{cm}^{-1}$, $T = 153\,\text{K}$. The final R value is 0.053 for 3346 independent reflections with $I > 3\sigma I$ and 414 parameters. Configuration of the two quaternary stereogenic centers in **1c** is known as (R) by chemical correlation. The intramolecular C–H···N distances are 2.55 and 2.61 Å. Crystal data of **1d**: $C_{44}H_{36}N_{10}$, M 704.84, triclinic, $P\bar{1}$, $a = 9.771(6)\,\text{Å}$, $b = 9.861(7)\,\text{Å}$, $c = 19.37(1)\,\text{Å}$, $\alpha = 84.57(4)°$, $\beta = 76.61(4)°$, $\gamma = 72.20(3)°$, $U = 1727(2)\,\text{Å}^3$, $D_c\ (Z = 2) = 1.355\,\text{g cm}^{-1}$, $\mu = 0.84\,\text{cm}^{-1}$, $T = 153\,\text{K}$. The final R value is 0.084 for 3966 independent reflections with $I > 3\sigma I$ and 487 parameters. Crystal data of **7**: $C_{16}H_{10}N_4$, M 258.28, monoclinic, $C2/c$, $a = 19.951(7)\,\text{Å}$, $b = 5.635(2)\,\text{Å}$, $c = 10.559(4)\,\text{Å}$, $\beta = 104.695(2)°$, $U = 1148.2(7)\,\text{Å}^3$, $D_c\ (Z = 4) = 1.494\,\text{g cm}^{-1}$, $\mu = 0.94\ \text{cm}^{-1}$, $T = 153\,\text{K}$. The final R value is 0.054 for 550 independent reflections with $I > 3\sigma I$ and 41 parameters. This molecule is located on the twofold axis.
18. Torsion angle of 96.8° was reported for the solid-state structure of 8,8′-biquinolyl **8**,[19] indicating that nearly perpendicular structure is intrinsic for these heterobiaryls **7** and **8** with two nitrogen atoms at *peri*-positions.
19. Lenner, M.; Lindgren, O. *Acta Crystallogr.* **1976**, *B32*, 1903.
20. (a) Buchen, T.; Hazell, A.; Jessen, L.; McKenzie, C. J.; Nielsen, L. P.; Pederson, J. Z.; Schollmeyer, D. *J. Chem. Soc., Dalton Trans.* **1997**, 2697; (b) Bock, H.; Göbel, I.; Näther, C.; Havlas, Z.; Gavezzotti, A.; Filippini, G. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1755.
21. (a) Rathore, R.; Lindeman, S. V.; Kumar, A. S.; Kochi, J. K. *J. Am. Chem. Soc.* **1998**, *120*, 6931; (b) Hünig, S.; Kemmer, M.; Wenner, H.; Barbosa, F.; Gescheidt, G.; Perepichka, I. F.; Bäuerle, P.; Emge, A.; Peters, K. *Chem. Eur. J.* **2000**, *6*, 2618.
22. Fungo, F.; Otero, L.; Durantini, E.; Thompson, W. J.; Silber, J. J.; Moore, T. A.; Moore, A. L.; Gust, D.; Sereno, L. *Phys. Chem. Chem. Phys.* **2003**, *5*, 469.
23. Shen, X.; Moriuchi, T.; Hirao, T. *Tetrahedron Lett.* **2003**, *44*, 7711.
24. Calcd for $C_{84}H_{64}F_{24}N_{18}P_4Ru_2$: C, 47.87; H, 3.06; N, 11.96. Found: C, 47.86; H, 3.03; N, 12.04.
25. Yamashita, Y.; Tomura, M.; Zaman, M. B.; Imaeda, K. *Chem. Commun.* **1998**, 1657.