Molbank **2010**, M677; doi:10.3390/M677

OPEN ACCESS

molbank

ISSN 1422-8599

www.mdpi.com/journal/molbank

Short Note

Tris{4-[(1,3-diphenyl-1*H*-pyrazol-4-yl)methylene]-4[1]-aminobiphenyl}amine

Sandhya P. Veettil and Karickal R. Haridas *

School of Chemical Science, Kannur University, Payyanur campus, (p.o) Edat, Kannur, Kerala, India

* Author to whom correspondence should be addressed; E-Mail: krharidas2001@yahoo.com.

Received: 25 February 2010 / Accepted: 31 March 2010 / Published: 20 April 2010

Abstract: Tris{4-[(1,3-diphenyl-1*H*-pyrazol-4-yl)methylene]-4[1]-aminobiphenyl}amine was synthesized from *N*-(4-bromophenyl)-*N*-[(1,3-diphenyl-1*H*-pyrazol-4-yl)methylene]amine and tris(4-bromophenyl)amine based on Ullmann coupling reaction. The synthesized compound was characterized by NMR, IR, MS and elemental analysis.

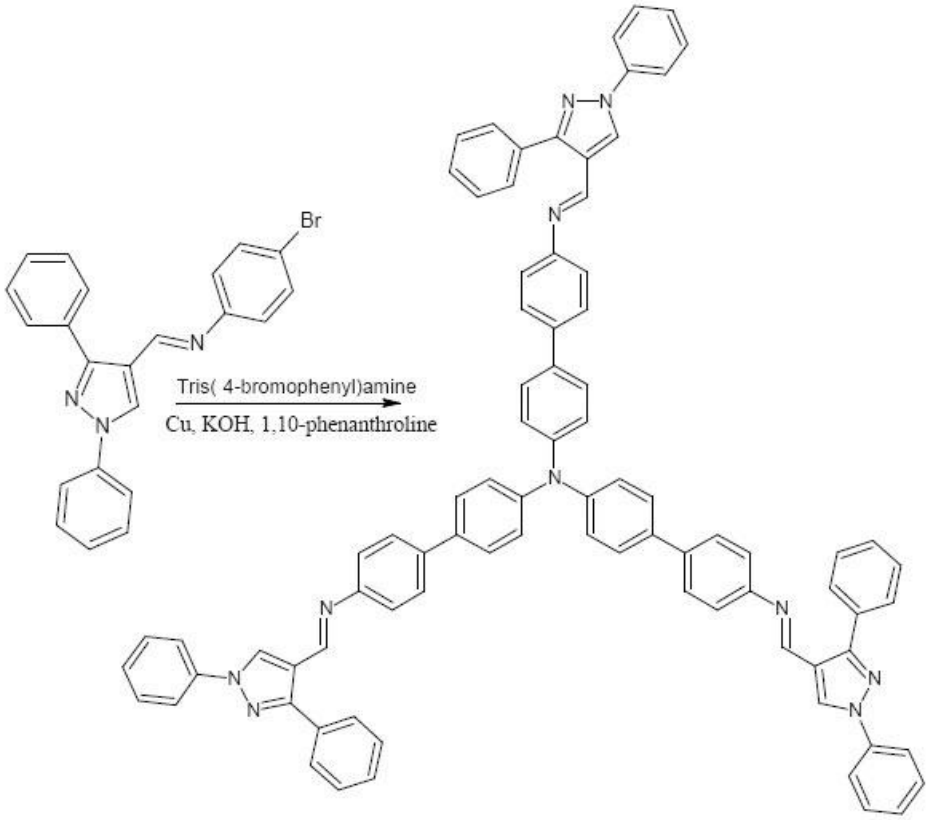
Keywords: 1,3-diphenyl-1*H*-pyrazole-4-carboxaldehyde; tris(4-bromophenyl)amine; Ullmann coupling

---

As part of a study towards the preparation of highly conjugated polyaromatcs incorporating a pyrazole motif with potential application in photovoltaic devices, the title compound tris{4-[(1,3-diphenyl-1*H*-pyrazol-4-yl)methylene]-4[1]-aminobiphenyl}amine is prepared. The triarylamine moiety fulfills the requirement of easy and reversible oxidation and therefore constitutes the building block of many of the hole-transporting materials [1].

Electrolytic copper (100 mg, 1.6 mmol), KOH (10 mg, 0.178 mmol) and 1,10-phenanthroline (1.0 mg, 0.006 mmol) were added to a stirred solution of *N*-(4-bromophenyl)-*N*-[(1,3-diphenyl-1*H*-pyrazol-4-yl)methylene]amine [2–4] (121 mg, 0.3 mmol) and tris(4-bromophenyl)amine (48 mg, 0.1 mmol) in anhydrous DMF. The resultant mixture was heated at 130 ℃ for 18 h and then filtered hot to remove the copper compounds and the base [5,6]. The solvent DMF was evaporated under vacuum and the dark brown solid was triturated with ethyl acetate, filtered and further purified by chromatography on silica gel, using ethyl acetate-hexane (1:4) as eluent. The product is most probably the *E* isomer, given the high degree of symmetry deduced from the ^{13}C NMR data and the ^{1}H NMR data which indicate there is only one product formed.

Scheme 1. Synthesis of tris{4-[(1,3-diphenyl-1*H*-pyrazol-4-yl)methylene]-4[1]-amino-biphenyl}amine.



Yield: 65%

M.p.: 128 ℃

IR (KBr) cm^{-1}: 2998 (Ar C-H_{str}), 1603 (C=N_{str}), 1452 (Ar C=C_{str}), 1337 (Ph-N_{str}), 1023 (Ar C-H_{def}).

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 10.23 (s, 3H, pyrazole 5-H), 8.72 (s, 3H, HC=N), 7.93–6.69 (m, 54H, Ar).

^{13}C NMR (75 MHz, DMSO-d_6): 158.0, 140.5, 139.0, 136.0, 129.1, 128.3, 127.0, 123.0, 118.0, 112.5, 106.0, 103.7.

MS: *m/z* (ES), 1209 [$(MH)^+$].

Elemental analysis calculated for $C_{84}H_{60}N_{10}$ (1208.5): C, 83.42%; H, 5.00%; N, 11.58%. Found: C, 84.32%; H, 5.25%; N, 11.43%.

Acknowledgement

We are thankful to NIIST, Thiruvanathapuram for recording NMR spectra.

References

1. Thelakkat, M.; Schmitz, C.; Hohle, C.; Strohriegl, P.; Schmidt, H.-W.; Hofmann, U.; Schloter, S.; Haarer, D. Novel functional materials based on triarylamines-synthesis and application in electroluminescent devices and photorefractive systems. *Phys. Chem. Chem. Phys.* **1999**, *1*, 1693–1698.
2. Sandhya, P.V.; Haridas, K.R. 1,3,5-Tris{[*N*-(1,3-diphenyl-1H-pyrazol-4-yl)methylene]-4-aminophenyl}benzene. *Molbank* **2009**, *2009*, M624.
3. Mohite, S.K.; Magdum, C.S. Novel synthesis of functionally substituted *N*-{[3-(4-chlorophenyl)-1-phenyl-1*H*-pyrazol-4-yl]methylene}anilines and their pharmacological screening. *Int. J. Chem. Sci*. **2006**, *4*, 980–988.
4. Rathelot, P.; Azas, N.; El-Kashef, H.; Delmas, F.; Di Giorgio, C.; Timon-David, P.; Maldonado, J.; Vanelle, P. 1,3-Diphenylpyrazoles: Synthesis and antiparasitic activities of azomethine derivatives. *Eur. J. Med. Chem.* **2002**, *37*, 671–679.
5. Goodbrand, H.B.; Hu, N.-X. Ligand-accelerated catalysis of the Ullmann condensation: Application to hole conducting triarylamines. *J. Org. Chem.* **1999**, *64*, 670–674.
6. Zhang, S.: Zhang, D.; Liebeskind, L.S. Ambient temperature, Ullmann-like reductive coupling of aryl, heteroaryl, and alkenyl halides. *J. Org. Chem.* **1997**, *62*, 2312–2313.