

Naphthalene proton sponges as hydride donors: diverse appearances of the *tert*-amino-effect

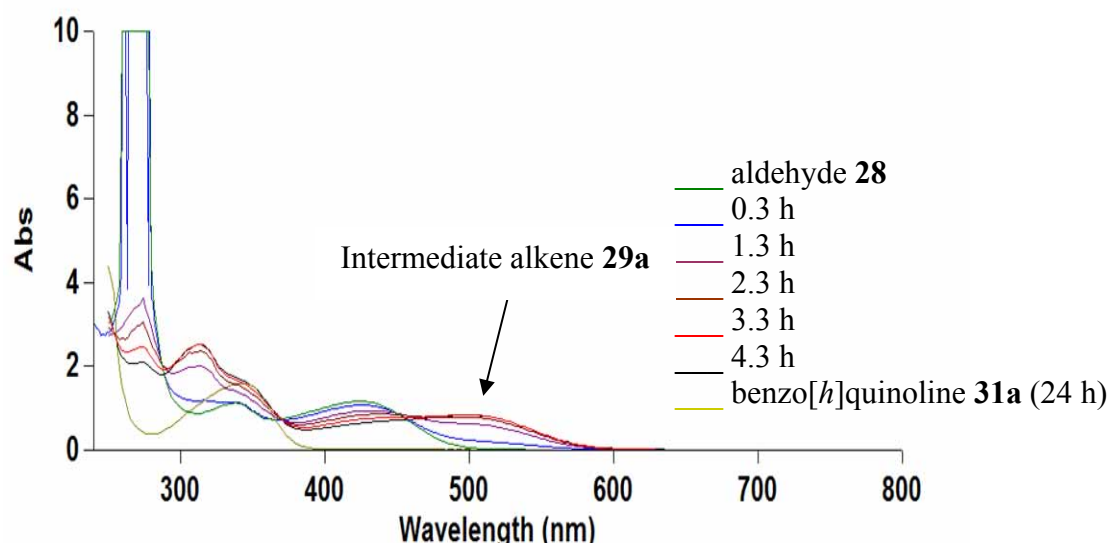
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Supporting information

Fig. S1 UV monitoring for the formation of **28** (**29a**) into **31a** in EtOH at room temperature.



Stereochemistry

Stereochemistry of 2-vinyl- and 2,7-divinyl-1,8-bis(dimethylamino)naphthalenes is a matter of interest because alkenes **29c,d,f**, **34a,c,d**, **39a,b** and **42a,b** can exist in *E*- or *Z*-form. X-ray data testify that at least for **29f** *E*-isomer is realized in the solid with the C $_{\alpha}$ -H bond pointing in the same direction as doing the NMe $_2$ group and with the more bulky 2-benzimidazolyl group in the *trans*-position to 2-naphthyl substituent. Apparently, this geometry is typical for all other alkenes both in the solid and in solution. This follows from considerable deshielding of the C $_{\alpha}$ -H hydrogen as compared with that for compound **34a** and from large 3J constants for vinylic hydrogens (Table S1).

Table S1 δ_{H} in 2-vinyl- and 2,7-divinyl-1,8-bis(dimethylamino)naphthalenes

Alkene	R ¹ , R ²	δ_{H} , ppm (3J , Hz)	Solvent
34a	CN, CN	7.84 ^a	CDCl ₃
29d, 34d	CN, CO ₂ Et	8.45, 8.39 ^a	CDCl ₃
29c, 34c	CN, Ts	8.37, 8.33 ^a	CDCl ₃
29f		8.66	CDCl ₃
		8.35	DMSO-d ₆
39a		8.03 (15.79)	DMSO-d ₆
		8.14 (15.96)	CD ₃ OD
39b		8.28 (15.48)	DMSO-d ₆

42a	H, NO ₂	8.40 (13.68)	CDCl ₃
42a ·HClO ₄	H, NO ₂	8.44 (13.33)	DMSO-d ₆
42b	Me, NO ₂	8.20	CDCl ₃
		8.16	CD ₃ OD
42b ·HClO ₄	Me, NO ₂	8.43	DMSO-d ₆

^a For the 2,7-divinyl derivative.

As regards to benzo[*h*]quinolines **31c–f** and quino[7,8:7',8']quinolines **35c,d** having one or two chiral atoms, they were isolated as a mixture of stereoisomers (Table S2). The ratio of diastereomers for **35c** and **35d** is near 1:1, although it could not be evaluated more precisely due to a strong overlapping of the diagnostic signals in the NMR spectra (*e.g.* C_{arom}–Me protons for **35c** and OCH₂Me ones for **35d**).

Table S2 ¹H and ¹³C NMR characteristics for the aliphatic protons of benzo[*h*]quinolines and quino[7,8:7',8']quinolines

Benzo[<i>h</i>]- quinolines and quino[7,8:7',8']- quinolines	δ ppm (ⁿ J/Hz)					Solvent
	2-CH ₂ , 11-CH ₂ ^a	3-C, 10-C ^a	4-CH ₂ , 9-CH ₂ ^a			
31a	3.98	57.01	25.80	3.63	37.58	CDCl ₃
31a ·HClO ₄	4.1	–	–	4.1	–	DMSO-d ₆
	4.3 (² J 14.0)			3.9 (² J 17.1)		
31b	3.7	–	–	3.4	–	CDCl ₃
31c	3.9 (² J 13.3)	53.3	22.3	3.2 (² J 16.4, ⁴ J 2.2)	33.7	CDCl ₃
	4.0 (² J 13.3)			3.8 (² J 16.4)		
31d	3.7 (² J 13.0)	–	–	3.4 (² J 16.4)	–	CDCl ₃
	3.9 (² J 13.2)			3.6 (² J 16.7)		
31e	3.70 (² J 13.02)	56.63	38.30	3.42 (² J 16.14)	35.82	CDCl ₃
	3.93 (² J 13.02)			3.64 (² J 16.50)		
31f	3.9	–	–	3.7 (² J 15.3)	–	DMSO-d ₆
	4.2 (² J 13.1)			3.9		
35a	3.8	55.8	26.5	3.0	37.2	CDCl ₃
	4.1			3.7 (² J 13.3)		DMSO-d ₆ ^b
35b	3.5–3.7	–	–	2.7–3.2	–	CDCl ₃
				3.5–3.7		
35c	3.6–4.1	52.8	22.3	3.2	33.6	CDCl ₃
				3.6–4.1		
35d	3.7	63.66	37.7	3.5 (² J 16.7)	36.3	CDCl ₃
	3.9	3.7		3.7		

^a For quino[7,8:7',8']quinolines.

^b For ¹³C NMR.

Fig. S2 ^1H - ^{13}C HSQC plots for **31a**.

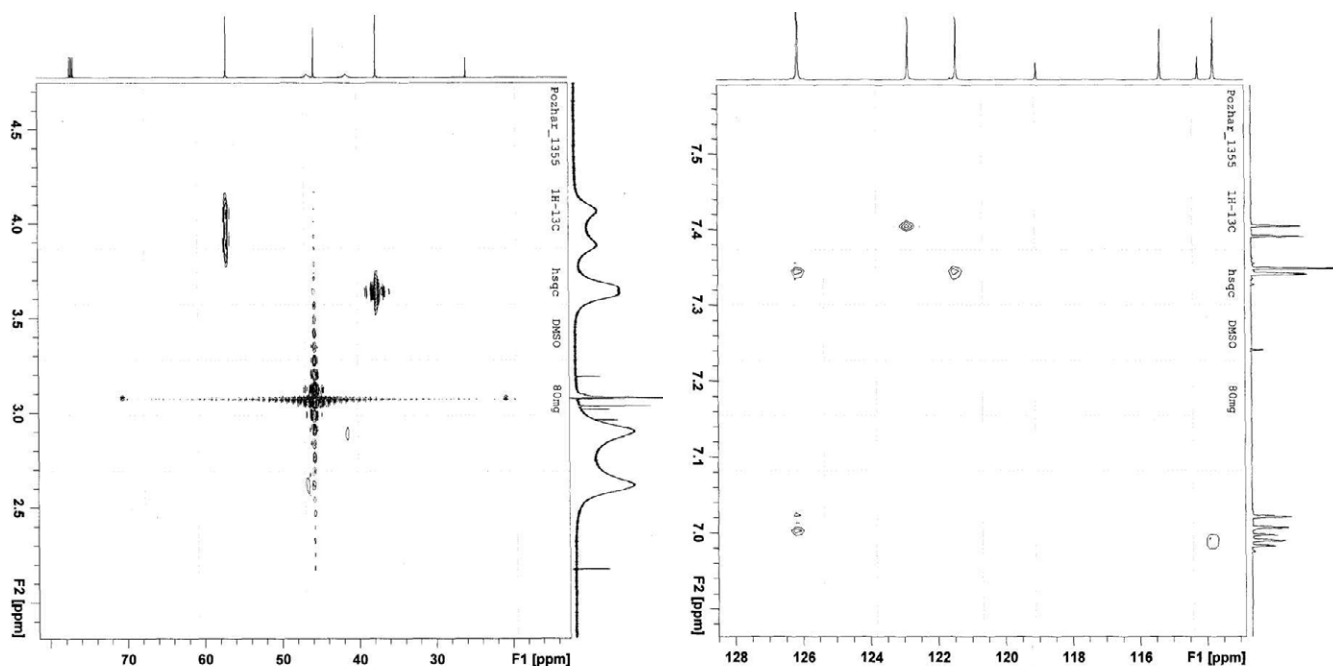
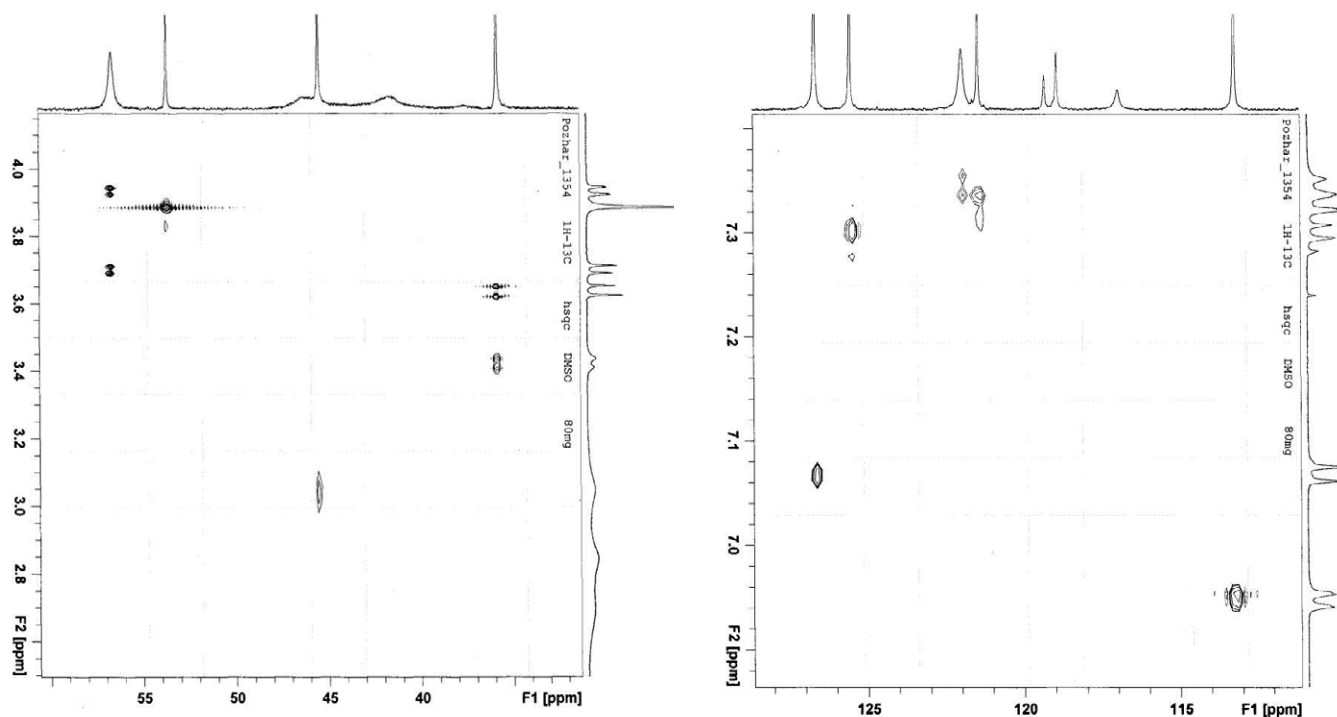


Fig. S3 ^1H - ^{13}C HSQC plots for **31e**.



Crystal structure of **29f**

Alkene **29f** demonstrates some peculiar type of intermolecular aggregation allowing to conclude that there are endless H-bonded chains along the *a* axis (Fig. S4). Though the NH proton was not

localised, these chains are undoubtedly arranged through the short contacts between the nitrogens of the benzimidazolyl groups.

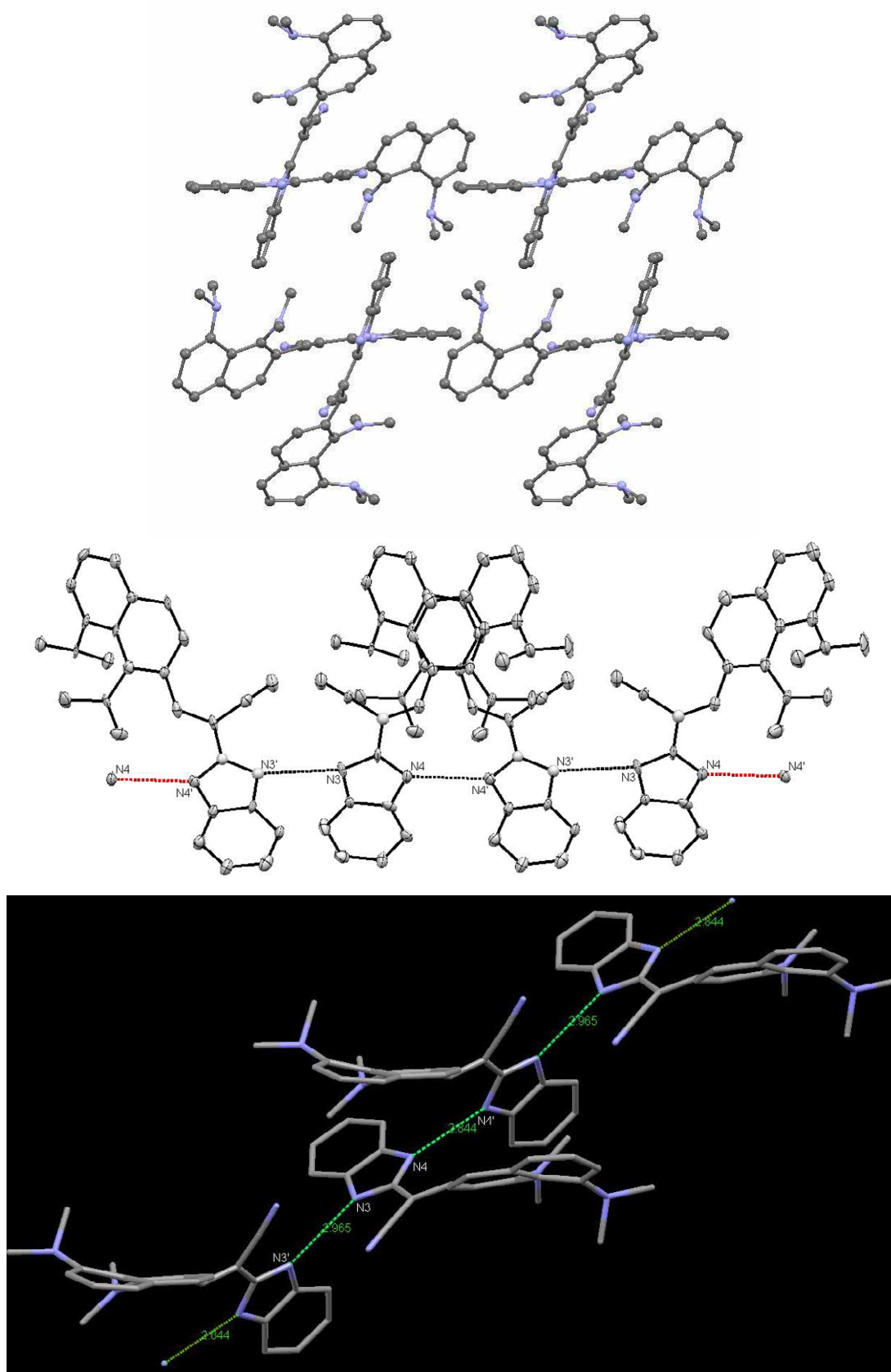


Fig. S4 Fragment of crystal structure of alkene **29f** (view down the *a* axis; above) showing close contacts between the imidazolyl nitrogens (middle) with indicated distances (below).

This is reminiscent with the mode of packing of unsubstituted benzimidazole (see below; BZDMAZ03 entry from CCDC), although here the H-bonded chains are more like a zigzag due to a co-planarity of back and forth situated imidazole rings.

