Turkish Journal of Chemistry

http://journals.tubitak.gov.tr/chem/

Research Article

Turk J Chem
(2018) 42: 1398 – 1407
© TÜBİTAK
doi:10.3906/kim-1806-68

Investigation of the hydrogen bond donating ability of 1,8-naphthalenediol by NMR spectroscopy and its use as a hydrogen bonding catalyst

Yunus Emre TÜRKMEN[1,2,*]

[1]Department of Chemistry, Faculty of Science, Bilkent University, Ankara, Turkey
[2]National Nanotechnology Research Center and Institute of Materials Science and Nanotechnology (UNAM), Bilkent University, Ankara, Turkey

Received: 28.06.2018 • **Accepted/Published Online:** 06.08.2018 • **Final Version:** 11.10.2018

Abstract: The hydrogen bond donating ability of 1,8-naphthalenediol was investigated via a series of ^{1}H, ^{13}C, and ^{31}P NMR experiments. Complexation studies using triphenylphosphine oxide and cyclohexanone as hydrogen bond acceptors revealed that 1,8-naphthalenediol is a more effective hydrogen bond donor compared to 1-naphthol and 8-methoxy-1-naphthol. Afterwards, its effectiveness as a hydrogen bonding catalyst was demonstrated in the Friedel–Crafts-type addition reaction of indole to *trans*-β-nitrostyrene.

Key words: Hydrogen bonding, 1,8-naphthalenediol, organocatalysis, phenols

1. Introduction

Hydrogen bonding and Brønsted acid catalysis are two important branches of organocatalysis, which attracted significant attention in organic synthesis in the past two decades.[1−7] In the former type of catalysis, noncovalent hydrogen bonding interaction between a hydrogen bond donor and a substrate leads to the activation of the substrate and results in an increase in reaction rate.[8] Among various types of hydrogen bond donor functional groups, alcohol and phenol derivatives found widespread use as hydrogen bonding catalysts.[9,10]

The use of phenol-based hydrogen bond donors as highly active organocatalysts dates back to the early 1980s when Hine and coworkers introduced biphenylenediols (**1**) as dual hydrogen bond donors through an elegant design (Figure 1).[11−14] After about two decades, Rawal and coworkers, in their pioneering studies, demonstrated that TADDOLs (**2**) are highly effective chiral hydrogen bonding catalysts for a variety of enantioselective transformations (Figure 1).[15−17] In 2003, PHANOL derivatives (**3**) were developed by Braddock and coworkers as paracyclophane-based dual hydrogen bonding catalysts.[18,19] Ar-BINMOLs (**4**), introduced by Lai, Guo, and coworkers in 2011, found applications as chiral ligands for metal-catalyzed asymmetric reactions and as organocatalysts.[20−22] In 2013, the performance of diarylacetylenediols[23,24] (**5**) as phenol-based, dual hydrogen bonding catalysts was investigated by the Rawal group (Figure 1).[25] More recently, Ertürk and coworkers described the use of chiral HAROLs (**6**) as hydrogen bonding catalysts in Morita–Baylis–Hillman reactions and as ligands for the enantioselective addition reactions of organometallic compounds to aldehydes (Figure 1).[26]

Despite the exciting developments in this area, discovery of new hydrogen bond donor scaffolds for

*Correspondence: yeturkmen@bilkent.edu.tr

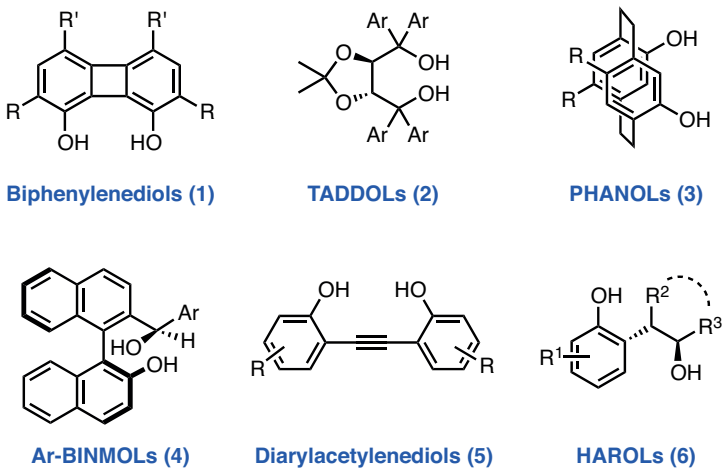


Figure 1. Selected examples of alcohol- and phenol-based hydrogen bonding catalysts.

use in organocatalysis is still a subject of extensive research. In this context, the diol motif present in 1,8-naphthalenediol (**7**) occurred as a potential candidate to be utilized in hydrogen bonding catalysis (Figure 2). Through IR spectroscopic studies, 1,8-naphthalenediol (**7**) was shown by Foti and coworkers to have the solution structure **7′**, in which one of the –OH groups participates in an intramolecular hydrogen bonding, whereas the second –OH hydrogen is available for an intermolecular hydrogen bonding interaction.[27] The presence of the intramolecular hydrogen bond in structure **7′** was demonstrated to increase the hydrogen bonding ability of the remaining free –OH group of 1,8-naphthalenediol (**7**).[27] Furthermore, this compound was found to have a high activity in hydrogen atom transfer (HAT) processes in radical reactions and exhibited significant antioxidant properties.[27–29] This type of increased hydrogen bond donating ability due to an intramolecular hydrogen bond[30] has been utilized efficiently in the area of hydrogen bonding catalysis.[17,31,32] In a computational study reported in 2013, the keto-enol tautomerization equilibria of various naphthols and 9-anthrols and the effect of hydrogen bonding on these equilibria were investigated by Korth and Mulder.[33] Finally, it should be noted that the first and second acid dissociation constants (pK_{a1} and pK_{a2}) for 1,8-naphthalenediol (**7**) in water were determined to be 6.71 and >13.00, respectively,[34] whereas 1-naphthol (**8**) has a pKa value of 9.22 in water.[35]

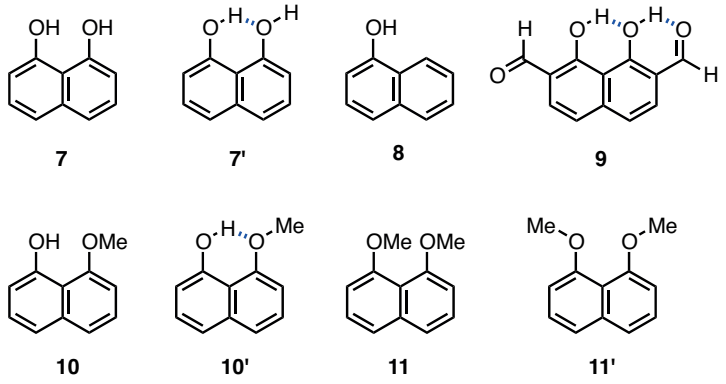


Figure 2. Structures of 1,8-naphthalenediol and naphthol derivatives.

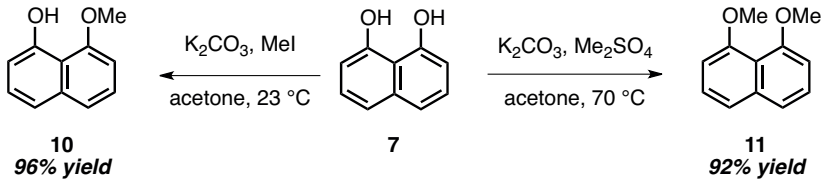
While the X-ray structure of 1,8-naphthalenediol (**7**) has not been reported, the crystal structure of

compound **9** was shown to display an intramolecular hydrogen bond between the two –OH groups of the 1,8-naphthalenediol core (Figure 2).[36] Due to all these reasons, 1,8-naphthalenediol (**7**) was expected to be a good candidate for an effective hydrogen bonding catalyst because of the increased hydrogen bond donating strength of the phenol groups.

In this study, the hydrogen bond donating ability of 1,8-naphthalenediol (**7**) has been investigated in detail using a variety of NMR spectroscopic techniques, and subsequently, its catalytic activity has been explored. During these studies, 8-methoxy-1-naphthol (**10**) and 1-naphthol (**8**) were tested as mono-phenol-containing hydrogen bond donors in control experiments (Figure 2). While compound **10** is expected to have a similar intramolecular hydrogen bond in its structure (**10′**), 1-naphthol (**8**) does not have this possibility, and its –OH group is available for an intermolecular hydrogen bonding interaction. Finally, 1,8-dimethoxynaphthalene (**11**) was used for comparison in control experiments. The reported X-ray structure of this compound (**11′**) indicates that the two $-CH_3$ groups lie in opposite directions, possibly to avoid steric repulsion.[37]

2. Results and discussion

Initially, 8-methoxy-1-naphthol (**10**)[38] and 1,8-dimethoxynaphthalene (**11**)[39] were prepared by mono- and di-methylation reactions starting from the commercially available 1,8-naphthalenediol (**7**) (Scheme). Whereas mono-methylation of **7** proceeds smoothly at 23 °C providing **10** in 96% yield, the second methylation requires refluxing the reaction mixture at 70 °C, and 1,8-dimethoxynaphthalene (**11**) was obtained in 92% yield. In the latter reaction, dimethyl sulfate (Me_2SO_4) was used as the methylating agent due to its higher boiling point compared to that of MeI. The requirement of a higher temperature for the second methylation reaction may be attributed to the decreased acidity of the –OH group of **10** due to the presence of an intramolecular hydrogen bond (structure **10′**).



Scheme. Preparation of 8-methoxy-1-naphthol (**10**) and 1,8-dimethoxynaphthalene (**11**).

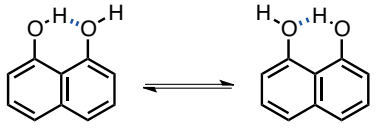
2.1. NMR studies

Hydrogen bond donating abilities of compounds **7**, **8**, and **10** were investigated using ^1H, ^{31}P, and ^{13}C NMR spectroscopic techniques. Initially, the ^1H NMR spectra of these three hydrogen bond donors (0.05 M) were recorded in $CDCl_3$ and DMSO-d_6, and the results were compared (Table 1). The chemical shift of the –OH hydrogen of 1-naphthol (**8**) was measured to be 5.28 ppm, which shifted downfield to 10.08 ppm when DMSO-d_6 was used as a solvent (Table 1, entry 1). $CDCl_3$ is not a good hydrogen bond acceptor solvent, and intermolecular hydrogen bonding between molecules of **8** is expected to be low at a concentration of 0.05 M. Therefore, the large chemical shift difference of 4.80 ppm can be attributed to the formation of strong hydrogen bonds between 1-naphthol (**8**) and DMSO-d_6 molecules. When a similar NMR experiment was performed using 8-methoxy-1-naphthol (**10**), the chemical shift dependence for the –OH hydrogen on the nature of solvent was found to be marginal (Table 1, entry 2). The chemical shift was observed to be 9.32 ppm in $CDCl_3$, which

supports the presence of an intramolecular hydrogen bond as shown in the structure of **10′** (Figure 2). In DMSO-d_6, the –OH hydrogen resonates at 9.37 ppm, corresponding to a $\Delta\delta$ value of 0.05 ppm. This result clearly indicates that the intramolecular hydrogen bond present in **10** decreases the hydrogen bond donating ability of this –OH group and therefore it is not available for further hydrogen bonding interaction with DMSO-d_6 molecules. Finally, ^{1}H-NMR spectra of 1,8-naphthalenediol (**7**) were recorded in $CDCl_3$ and DMSO-d_6, again at a concentration of 0.05 M (Table 1, entry 3). The –OH hydrogens of compound **7** give only one singlet signal at 7.83 ppm at $CDCl_3$. This can be explained by a rapid equilibrium between **7′** and **7″** (Table 1) so that the chemical shift of 7.83 ppm may be considered as an average of intramolecularly hydrogen-bonded and free –OH groups. When the ^{1}H-NMR spectrum of **7** was recorded in DMSO-d_6, the chemical shift of the –OH hydrogens was observed to be 10.83 ppm, resulting from the intermolecular hydrogen bonds between compound **7** and DMSO-d_6 molecules.

Table 1. Investigation of the chemical shifts of O-H hydrogens in the ^{1}H NMR spectra of **7**, **8**, and **10** (0.05 M) in $CDCl_3$ and DMSO-d_6.

Entry	Hydrogen bond donor	δ(O-H) in $CDCl_3$ (ppm)	δ(O-H) in DMSO-d_6 (ppm)	$\Delta\delta$ (ppm)
1	**8**	5.28	10.08	4.80
2	**10**	9.32	9.37	0.05
3	**7**	7.83	10.83	3.00



After the initial studies, the hydrogen bonding interaction between 1,8-naphthalenediol (**7**) and triphenylphosphine oxide (**12**) was investigated by ^{31}P{^{1}H} NMR spectroscopy along with comparison using monophenol derivatives **8** and **10** as well as 1,8-dimethoxynaphthalene (**11**). The singlet signal observed at 29.71 ppm in the ^{31}P NMR spectrum of triphenylphosphine oxide (**12**) in $CDCl_3$ (0.10 M) shifts to 32.95 ppm in a 1:1 mixture of 1,8-naphthalenediol (**7**) and **12** at the same concentration ($\Delta\delta$ = 3.24 ppm; Table 2, entries 1 and 2). However, when the ^{31}P NMR spectrum of a 1:2 mixture of **12** and **10** was recorded ([**12**] = 0.10 M), the singlet signal was observed to be at 29.69 ppm, which further supports that the intramolecularly bonded –OH group of **10** does not participate in an additional hydrogen bonding interaction (Table 2, entry 3). The ^{31}P NMR spectrum of a solution of **12** and 1-naphthol (**8**) (1:2 ratio, [**12**] = 0.10 M) in $CDCl_3$ exhibited a signal at 32.04 ppm that corresponds to a $\Delta\delta$ value of 2.33 ppm (Table 2, entry 4). When compared to the result obtained with 1,8-naphthalenediol (**7**), this result clearly demonstrates that compound **7** is a better hydrogen bond donor than 1-naphthol (**8**). Finally, 1,8-dimethoxynaphthalene (**11**) was used in a control experiment. As expected, compound **11**, which lacks strong hydrogen bond donors, did not lead to any significant change in the ^{31}P NMR spectrum of triphenylphosphine oxide (**12**) when **11** and **12** were mixed in 1:2 ratio (Table 2, entry 5). The stacked ^{31}P NMR spectra for these experiments are shown in Figure 3.

After the completion of the ^{31}P NMR studies, the hydrogen bonding interactions of compounds **7**, **8**, and **10** with a carbonyl group were examined using ^{13}C NMR spectroscopy. To this end, cyclohexanone (**13**)

Table 2. Investigation of the chemical shift of the phosphorus of triphenylphosphine oxide (**12**) in the ^{31}P NMR spectra upon addition of **7**, **8**, **10**, and **11** in $CDCl_3$.

Entry	Hydrogen bond (HB) donor	Ph_3PO: HB Donor	δ(P=O) (ppm)	$\Delta\delta$ (ppm)
1	-	-	29.71	-
2	**7**	1:1	32.95	3.24
3	**10**	1:2	29.69	–0.02
4	**8**	1:2	32.04	2.33
5	**11**	1:2	29.67	–0.04

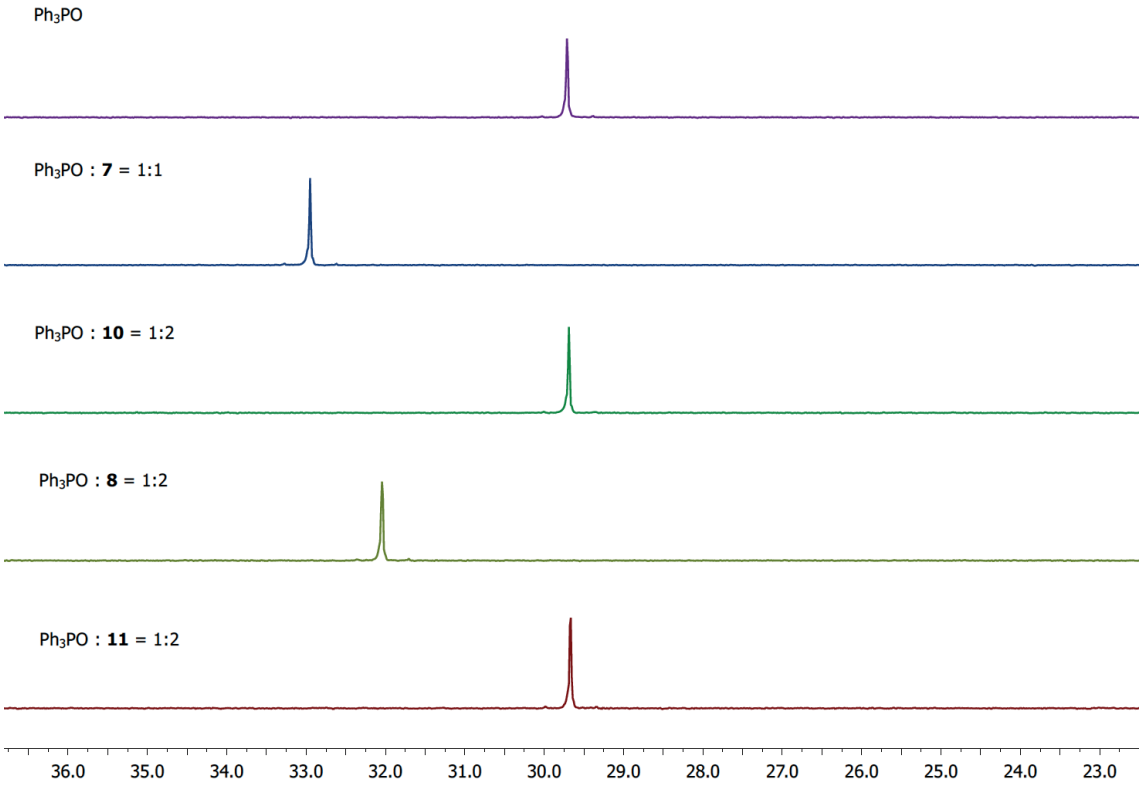


Figure 3. Stacked ^{31}P NMR spectra when triphenylphosphine oxide (**12**) was used as the hydrogen bond acceptor.

was selected as the hydrogen bond acceptor to be used in this study. The C=O carbon of cyclohexanone (**13**) resonates at 212.20 ppm in $CDCl_3$ (0.10 M) (Table 3, entry 1). This signal was observed to undergo a downfield shift to 214.46 ppm ($\Delta\delta$ = 2.26 ppm) when **13** was mixed with 1,8-naphthalenediol (**7**) in a 1:1 ratio (0.10 M) in $CDCl_3$, which is indicative of a strong hydrogen bonding interaction (Table 3, entry 2). In accordance with the previous observations, 8-methoxy-1-naphthol (**10**) does not act as a strong hydrogen bond donor, and the chemical shift of **13** showed almost no change when **13** and **10** were mixed in 1:2 ratio (Table 3, entry 3). When the ^{13}C NMR spectrum of a 1:2 mixture of cyclohexanone (**13**) and 1-naphthol (**8**) was recorded in $CDCl_3$ ([**13**] = 0.10 M), the chemical shift of the C=O carbon was found to be 213.80 ppm ($\Delta\delta$ = 1.60 ppm; Table 3, entry 4). This result once again shows that 1-naphthol (**8**) is capable of acting as a hydrogen bond donor

but less effectively than 1,8-naphthalenediol (**7**). Finally, the use of 1,8-dimethoxynaphthalene (**11**) in a control experiment did not result in any major change in the chemical shift of the C=O carbon of cyclohexanone (**13**) (Table 3, entry 5). The stacked ^{13}C NMR spectra showing the expanded region for this signal are presented in Figure 4.

Table 3. Investigation of the chemical shift of C=O carbon of cyclohexanone (**13**) in ^{13}C NMR spectra upon addition of **7**, **8**, **10**, and **11** in $CDCl_3$.

Entry	Hydrogen bond (HB) donor	Ph_3PO: HB Donor	δ(P=O) (ppm)	$\Delta\delta$ (ppm)
1	-	-	212.20	-
2	**7**	1:1	214.46	2.26
3	**10**	1:2	212.17	–0.03
4	**8**	1:2	213.80	1.60
5	**11**	1:2	212.15	–0.05

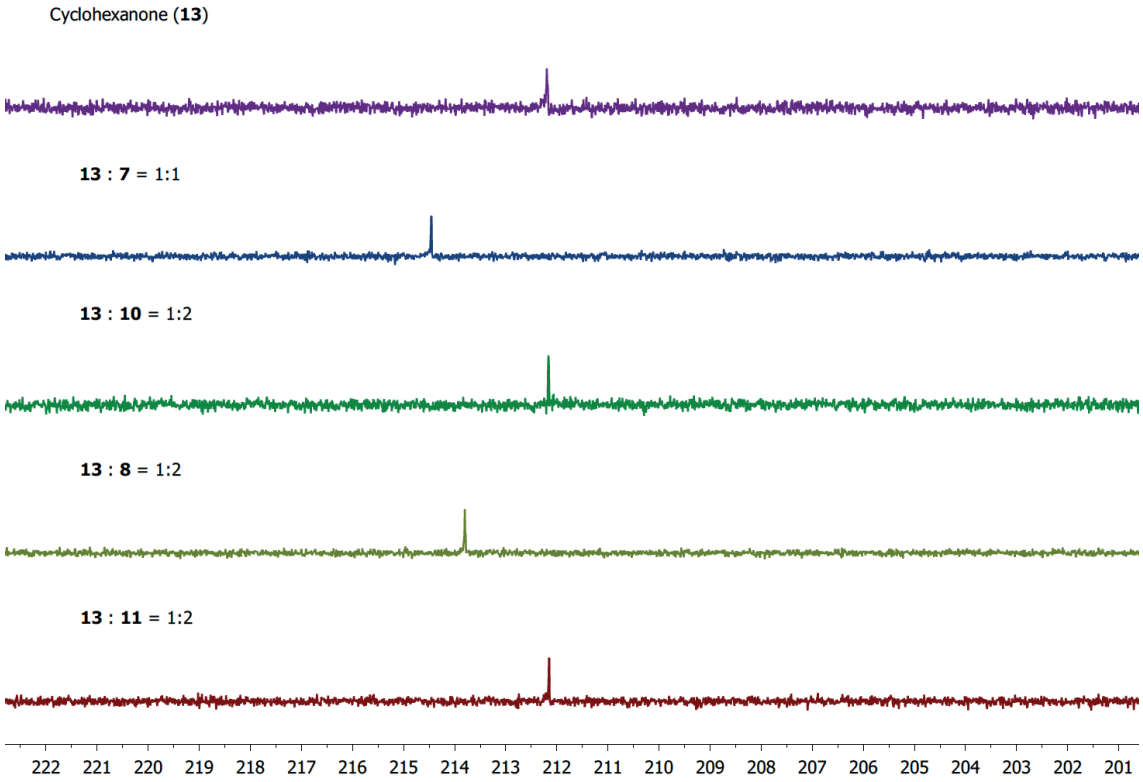


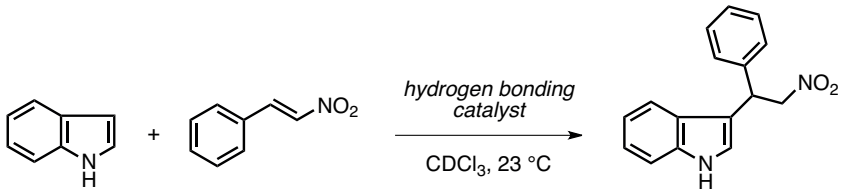
Figure 4. Stacked ^{13}C NMR spectra showing the signal for C=O carbon when cyclohexanone (**13**) was used as the hydrogen bond acceptor.

2.2. Catalytic studies

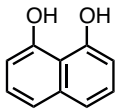
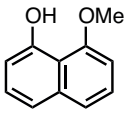
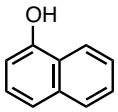
Encouraged by the results obtained from the NMR studies, the use of 1,8-naphthalenediol (**7**) as a hydrogen bonding catalyst was investigated next. For this purpose, the Friedel–Crafts-type addition of indole (**14**) to

trans-β-nitrostyrene (**15**) was selected as the test reaction (Table 4). It was shown that this reaction can be efficiently promoted using a variety of hydrogen bonding catalysts such as thioureas, ureas, thiophosphoric triamides, silanediols, and 1,3-disiloxanediols as well as in hydrogen bond donor solvents.[40–49] As shown in Table 4, all reactions in the present study were performed as duplicates in $CDCl_3$ at 23 °C, and the ratio of indole (**14**) to *trans*-β-nitrostyrene (**15**) was kept constant at 1:1.5 ([**14**] = 1.0 M). Initially, the background reaction between **14** and **15** in the absence of a catalyst was tested and it was found to be extremely slow at 23 °C. Under these conditions, adduct **16** was formed in only 2% conversion even after 72 h (Table 4, entry 1). Pleasingly, 1,8-naphthalenediol (**7**) proved to be an active catalyst for this transformation when used in 10 mol% catalyst loading, and the conversion to adduct **16** was found to be 43% (Table 4, entry 2). Next, monophenol-containing hydrogen bond donors **10** and **8** were tested as catalysts. With 20 mol% loading, compound **10** was much less active as a catalyst, providing adduct **16** with only 4% conversion (Table 4, entry 3). When 1-naphthol (**8**) was tested with 20 mol% loading, the conversion was observed to be 25% (Table 4, entry 4). It can be concluded from this result that while 1-naphthol (**8**) is a competent catalyst for the tested reaction, it is significantly less active compared to 1,8-naphthalenediol (**7**).

Table 4. Catalytic studies on the Friedel–Crafts-type addition of indole (**14**) to *trans*-β-nitrostyrene (**15**).[a]



14 **15** **16**

Entry	Hydrogen Bonding Catalyst	Catalyst Loading (%)	Conversion (%) after 72 h[b]
1	-	-	2
2	 **7**	10	43
3	 **10**	20	4
4	 **8**	20	25

[a] Reactions were carried out using 1.0 mmol of indole (**14**), 1.50 mmol of *trans*-β-nitrostyrene (**15**), 0.10 or 0.20 mmol of the hydrogen bonding catalyst, and 1.0 mL of $CDCl_3$. [b] Average of two experiments and determined by ^{1}H NMR spectroscopy.

2.3. Conclusions

In summary, the hydrogen bond donating ability of 1,8-naphthalenediol (**7**) was investigated via a series of ^{1}H, ^{13}C, and ^{31}P NMR experiments. 1,8-Naphthalenediol (**7**) was demonstrated to be a more effective hydrogen bond donor compared to 1-naphthol (**8**) in complexation experiments with triphenylphosphine oxide (**12**) and cyclohexanone (**13**), possibly due to the presence of an intramolecular hydrogen bond within its structure. Control experiments indicated the ineffectiveness of 8-methoxy-1-naphthol (**10**) and 1,8-dimethoxynaphthalene (**11**) in these complexation studies. Finally, the use of 1,8-naphthalenediol (**7**) as a hydrogen bonding catalyst was examined in the Friedel–Crafts-type addition reaction of indole (**14**) to *trans*-β-nitrostyrene (**15**). Studies on the development of more active hydrogen bonding catalysts with 1,8-naphthalenediol skeletons are currently underway in our laboratory.

3. Experimental

Analyses by thin-layer chromatography (TLC) were carried out using aluminum-backed plates precoated with silica gel (Merck, 60 Å, F_{254}). Flash column chromatographic purifications were performed using Silicycle 40–63 μm (230-400 mesh) silica gel. ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz), and ^{31}P NMR (162 MHz) spectra were recorded using a Bruker Avance 400 spectrometer in $CDCl_3$ and DMSO-d_6. Residual solvent signals (chloroform at 7.26 ppm and dimethyl sulfoxide at 2.50 ppm for ^{1}H NMR spectra; chloroform at 77.16 ppm for ^{13}C NMR spectra) were used for the calibration of NMR spectra. In ^{31}P NMR experiments, 85% aqueous H_3PO_4 solution was used as an external reference (0.0 ppm). High-resolution mass spectrometry (HRMS) data were obtained using an Agilent Technologies TOF (time-of-flight) LC/MS instrument. FTIR spectra were acquired using a Bruker Alpha-Platinum-ATR spectrometer. All commercially available reagents were used without further purification unless stated otherwise.

3.1. 8-Methoxy-1-naphthol (10)

The synthesis procedure was modified based on a literature report.[38] 1,8-Naphthalenediol (**7**) (200 mg, 1.25 mmol) was dissolved in 10 mL of acetone, and K_2CO_3 (207 mg, 1.50 mmol) and CH_3I (117 μL, 1.88 mmol) were added sequentially at rt. The resulting heterogeneous mixture was stirred at this temperature for 24 h. It was then quenched with H_2O (5 mL) and saturated with NH_4Cl solution (5 mL). The aqueous phase was extracted with EtOAc (2 × 10 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by flash column chromatography (EtOAc:hexane = 1:19) gave pure **10** (210 mg, 96%) as a white solid. All spectral data are in accordance with the reported values in the literature.[38] R_f = 0.51 (EtOAc:hexane = 1:9); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.32 (1H, s), 7.43 (1H, dd, J = 8.3, 0.4 Hz), 7.36 (1H, t, J = 8.0 Hz), 7.33–7.29 (2H, m), 6.88 (1H, dd, J = 7.4, 1.2 Hz), 6.78 (1H, d, J = 7.7 Hz), 4.06 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.3, 154.6, 136.9, 127.8, 125.7, 122.0, 119.0, 115.2, 110.5, 104.0, 56.2; FTIR (ATR, solid) 3352, 3051, 2951, 2844, 1629, 1609, 1580, 1513, 1451, 1397, 1307, 1227 cm^{-1}; HRMS (APCI+) calcd for $C_{11}H_{11}O_2$ $[M+H]^+$: 175.0754, found: 175.0759.

3.2. 1,8-Dimethoxynaphthalene (11)

The synthesis procedure has been modified based on a literature report.[39] 1,8-Naphthalenediol (**7**) (200 mg, 1.25 mmol) was dissolved in 10 mL of acetone, and K_2CO_3 (1.73 g, 12.5 mmol) and Me_2SO_4 (1.19 mL, 12.5

mmol) were added sequentially at rt. The resulting heterogeneous mixture was heated to 70 °C and stirred at this temperature for 24 h. It was then cooled down to rt and quenched with H_2O (15 mL). The aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and filtered. Concentration under reduced pressure gave pure **11** (216 mg, 92%) as a light yellow solid. All spectral data are in accordance with the reported values in the literature.[39] R_f = 0.46 (EtOAc:hexane = 1:9); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (2H, dd, J = 8.2, 1.4 Hz), 7.39–7.35 (2H, m), 6.86 (2H, dd, J = 7.4, 1.2 Hz), 3.99 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 137.5, 126.5, 121.0, 117.8, 106.3, 56.6; FTIR (ATR, solid) 3001, 2956, 2836, 1580, 1460, 1427, 1386, 1348, 1273, 1237 cm^{-1}; HRMS (APCI+) calcd for $C_{12}H_{13}O_2$ $[M+H]^+$: 189.0911, found: 189.0917.

3.3. General procedure for the addition of indole (14) to *trans*-β-nitrostyrene (15) catalyzed by the hydrogen bond donors

In these experiments, $CDCl_3$ was passed through a plug of K_2CO_3 prior to use in order to remove any potential acid that might be present. In a 20-mL vial, *trans*-β-nitrostyrene (**15**) (224 mg, 1.50 mmol) was dissolved in 1.0 mL of $CDCl_3$. Indole (**14**) (117 mg, 1.0 mL) and the hydrogen bonding catalyst (0.10 mmol **7**, 0.20 mmol **8**, or 0.20 mmol **10**) were added sequentially, and the resulting clear solution was stirred at 23 °C for 72 h. At the end of this time, 50 μL of the reaction solution was taken via a microsyringe and mixed with 0.5 mL of $CDCl_3$. The progress of the reaction was analyzed by ^{1}H NMR spectroscopy. The conversion values were determined through the comparison of the integration values for the signal of adduct **16** at 7.04 ppm[46] and the signal of indole (**14**) at 6.57 ppm.

References

1. McGilvra, J. D.; Gondi, V. B.; Rawal, V. H. In *Enantioselective Organocatalysis*; Dalko, P. I., Ed. Wiley-VCH: Weinheim, Germany, 2007, pp. 189-254.
2. Doyle, A. G.; Jacobsen, E. N. *Chem. Rev.* **2007**, *107*, 5713-5743.
3. Akiyama, T. *Chem. Rev.* **2007**, *107*, 5744-5758.
4. Connon, S. J. *Chem. Commun.* **2008**, *0*, 2499-2510.
5. Terada, M. *Synthesis* **2010**, 1929-1982.
6. Cheon, C. H.; Yamamoto, H. *Chem. Commun.* **2011**, *47*, 3043-3056.
7. Mahlau, M.; List, B. *Angew. Chem. Int. Ed.* **2013**, *52*, 518-533.
8. Jensen, K. H.; Sigman, M. S. *J. Org. Chem.* **2010**, *75*, 7194-7201.
9. Türkmen, Y. E.; Zhu, Y.; Rawal, V. H. In *Comprehensive Enantioselective Organocatalysis, Vol. 2*; Dalko, P. I., Ed. Wiley-VCH: Weinheim, Germany, 2013, pp. 239-288.
10. Türkmen, Y. E. In *Nonnitrogenous Organocatalysis*; Harned, A. M., Ed. CRC Press, Taylor & Francis: Boca Raton, FL, USA, 2018, pp. 13-37.
11. Hine, J.; Ahn, K.; Gallucci, J. C.; Linden, S. M. *J. Am. Chem. Soc.* **1984**, *106*, 7980-7981.
12. Hine, J.; Linden, S. M.; Kanagasabapathy, V. M. *J. Am. Chem. Soc.* **1985**, *107*, 1082-1083.
13. Hine, J.; Linden, S. M.; Kanagasabapathy, V. M. *J. Org. Chem.* **1985**, *50*, 5096-5099.
14. Kelly, T. R.; Meghani, P.; Ekkundi, V. S. *Tetrahedron Lett.* **1990**, *31*, 3381-3384.
15. Huang, Y.; Unni, A. K.; Thadani, A. N.; Rawal, V. H. *Nature* **2003**, *424*, 146-146.

16. Thadani, A. N.; Stankovic, A. R.; Rawal, V. H. *P. Natl. Acad. Sci. USA* **2004**, *101*, 5846-5850.
17. McGilvra, J. D.; Unni, A. K.; Modi, K.; Rawal, V. H. *Angew. Chem. Int. Ed.* **2006**, *45*, 6130-6133.
18. Braddock, D. C.; MacGilp, I. D.; Perry, B. G. *Synlett* **2003**, 1121-1124.
19. Braddock, D. C.; MacGilp, I. D.; Perry, B. G. *Adv. Synth. Catal.* **2004**, *346*, 1117-1130.
20. Gao, G.; Gu, F. L.; Jiang, J. X.; Jiang, K.; Sheng, C. Q.; Lai, G. Q.; Xu, L. W. *Chem. Eur. J.* **2011**, *17*, 2698-2703.
21. Gao, G.; Bai, X. F.; Yang, H. M.; Jiang, J. X.; Lai, G. Q.; Xu, L. W. *Eur. J. Org. Chem.* **2011**, *2011*, 5039-5046.
22. Zheng, L. S.; Jiang, K. Z.; Deng, Y.; Bai, X. F.; Gao, G.; Gu, F. L.; Xu, L. W. *Eur. J. Org. Chem.* **2013**, *2013*, 748-755.
23. Saied, O.; Simard, M.; Wuest, J. D. *Organometallics* **1996**, *15*, 2345-2349.
24. Saied, O.; Simard, M.; Wuest, J. D. *J. Org. Chem.* **1998**, *63*, 3756-3757.
25. Türkmen, Y. E.; Rawal, V. H. *J. Org. Chem.* **2013**, *78*, 8340-8353.
26. Dilek, Ö.; Tezeren, M. A.; Tilki, T.; Ertürk, E. *Tetrahedron* **2018**, *74*, 268-286.
27. Foti, M. C.; Barclay, L. R. C.; Ingold, K. U. *J. Am. Chem. Soc.* **2002**, *124*, 12881-12888.
28. Foti, M. C.; Johnson, E. R.; Vinqvist, M. R.; Wright, J. S.; Barclay, L. R. C.; Ingold, K. U. *J. Org. Chem.* **2002**, *67*, 5190-5196.
29. Manini, P.; Bietti, M.; Galeotti, M.; Salamone, M.; Lanzalunga, O.; Cecchini, M. M.; Reale, S.; Crescenzi, O.; Napolitano, A.; De Angelis, F. et al. *ACS Omega* **2018**, *3*, 3918-3927.
30. Dominelli-Whiteley, N.; Brown, J. J.; Muchowska, K. B.; Mati, I. K.; Adam, C.; Hubbard, T. A.; Elmi, A.; Brown, A. J.; Bell, I. A. W.; Cockroft, S. L. *Angew. Chem. Int. Ed.* **2017**, *56*, 7658-7662.
31. Hasegawa, A.; Naganawa, Y.; Fushimi, M.; Ishihara, K.; Yamamoto, H. *Org. Lett.* **2006**, *8*, 3175-3178.
32. Moriyama, K.; Sugiue, T.; Saito, Y.; Katsuta, S.; Togo, H. *Adv. Synth. Catal.* **2015**, *357*, 2143-2149.
33. Korth, H. G.; Mulder, P. *J. Org. Chem.* **2013**, *78*, 7674-7682.
34. Musso, H.; Matthies, H. G. *Chem. Ber.* **1961**, *94*, 356-368.
35. Pines, E.; Magnes, B. Z.; Lang, M. J.; Fleming, G. R. *Chem. Phys. Lett.* **1997**, *281*, 413-420.
36. Chen, Y. T.; Wu, P. J.; Peng, C. Y.; Shen, J. Y.; Tsai, C. C.; Hu, W. P.; Chou, P. T. *Phys. Chem. Chem. Phys.* **2017**, *19*, 28641.
37. Cosmo, R.; Hambley, T. W.; Sternhell, S. *Acta Cryst.* **1990**, *B46*, 557-562.
38. Fan, Y.; Feng, P.; Liu, M.; Pan, H.; Shi, Y. *Org. Lett.* **2011**, *13*, 4494-4497.
39. Yang, Y.; Lowry, M.; Xu, X.; Escobedo, J. O.; Sibrian-Vazquez, M.; Wong, L.; Schowalter, C. M.; Jensen, T. J.; Fronczek, F. R.; Warner, I. M. et al. *P. Natl. Acad. Sci. USA* **2008**, *105*, 8829-8834.
40. Dessole, G.; Herrera, R. P.; Ricci, A. *Synlett* **2004**, 2374-2378.
41. Herrera, R. P.; Sgarzani, V.; Bernardi, L.; Ricci, A. *Angew. Chem. Int. Ed.* **2005**, *44*, 6576-6579.
42. Fleming, E. M.; McCabe, T.; Connon, S. J. *Tetrahedron Lett.* **2006**, *47*, 7037-7042.
43. Ganesh, M.; Seidel, D. *J. Am. Chem. Soc.* **2008**, *130*, 16464-16465.
44. Rodriguez, A. A.; Yoo, H.; Ziller, J. W.; Shea, K. J. *Tetrahedron Lett.* **2009**, *50*, 6830-6833.
45. So, S. S.; Burkett, J. A.; Mattson, A. E. *Org. Lett.* **2011**, *13*, 716-719.
46. Schafer, A. G.; Wieting, J. M.; Mattson, A. E. *Org. Lett.* **2011**, *13*, 5228-5231.
47. Diemoz, K. M.; Hein, J. E.; Wilson, S. O.; Fettinger, J. C.; Franz, A. K. *J. Org. Chem.* **2017**, *82*, 6738-6747.
48. Gu, Y.; Barrault, J.; Jérôme, F. *Adv. Synth. Catal.* **2008**, *350*, 2007-2012.
49. Tang, R. J.; Milcent, T.; Crousse, B. *RSC Adv.* **2018**, *8*, 10314-10317.