dissolved in 20 mL of THF is slowly added within 1 h to a well-stirred suspension of $SmCp_2$ (10 mmol) in THF (150 mL) at -20 °C. A brown suspension is obtained. A solution of 4.16 mmol of aldehyde in 5 mL of THF is quickly added. The reaction mixture turns immediately yellow. After 2 h, the solution is treated as previously. Pure α-ketol is analyzed by GC, GC/MS, and ^1H NMR spectroscopy. In another series of experiments (Barbier-type conditions), acid chloride (4.16 mmol) and aldehyde (4.16 mmol) are mixed together in THF (5 mL) and added to a suspension of $SmCp_2$ (10 mmol) in THF (150 mL) at -20 °C.

2,2-Dimethyl-4-hydroxy-3-decanone: ^1H NMR δ 4.5 (m, 1 H), 3.3 (m, 1 H), 1.6 (m, 10 H), 1.20 (s, 9 H), 0.95 (t, J = 7.8 Hz, 3 H); ^{13}C NMR δ 217.9, 72.3, 42.5, 34.8, 31.6, 29.0, 26.7, 25.0, 22.5, 13.9; MS 200 (0.4) M^+, 115 (26.2) $C_6H_{13}CHOH$, 97 (65.7) C_7H_{13}, 85 (6.1) t-BuCO, 57 (100) t-Bu. Anal. Calcd for $C_{12}H_{24}O_2$: C, 71.95; H, 12.08. Found: C, 71.69; H, 11.85.

3,3-Dimethyl-1-hydroxy-1-phenyl-2-butanone: ^1H NMR δ 7.3 (m, 5 H), 5.4 (s, 1 H), 4.4 (m, 1 H), 1.05 (s, 9 H); MS 192 (0.4) M^+, 164 (7.4) M-CO, 107 (100) C_6H_5CHOH, 77 (31) C_6H_5, 57 (51.1) t-Bu. Anal. Calcd for $C_{12}H_{16}O_2$: 74.97; H, 8.38. Found: C, 74.78; H, 8.20.

2,2-Dimethyl-4-hydroxy-3-hexanone: ^1H NMR δ 4.5 (m, 1 H), 3.6 (m, 1 H), 1.6 (m, 2 H), 1.2 (s, 9 H), 0.95 (t, J = 7.9 Hz, 3 H); MS 144 (0.6) M^+, 88 (4.0), 69 (2.7), 57 (100) t-Bu. Anal. Calcd for $C_8H_{16}O_2$: C, 66.63; H, 11.18. Found: C, 66.58; H, 11.38.

1-Adamantyl-2-hydroxy-1-butanone: ^1H NMR δ 4.45 (t + s, 1 H), 3.3 (m, 1 H), 1.75 (m, 17 H), 0.9 (t, J = 8.1, Hz, 3 H); MS 222 (3.16) M^+, 193 (0.58) AdCOCHOH, 163 (5.42) AdCO, 135 (100) Ad; IR 3478, 1695, 1452, 1403, 1381. Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.50; H, 9.76.

1-Adamantyl-2-hydroxy-2-phenylethanone: ^1H NMR δ 7.35 (m, 5 H), 5.4 (s, 1 H), 4.4 (s, 1 H), 1.6 (m, 15 H); MS 270 (0.3) M^+, 163 (13.1) AdCO, 107 (12.9) PhCHOH, 77 (17.9) Ph. Anal. Calcd for $C_{18}H_{22}O_2$: C, 80.00; H, 8.15. Found: C, 80.08; H, 8.02.

1-Cyclohexyl-2-hydroxy-1-butanone: ^1H NMR δ 4.31 (m, 1 H), 3.40 (m, 1 H), 2.38 (m, 1 H), 1.6 (m, 12 H), 0.93 (t, J = 8.4 Hz, 3 H); MS 170 (1.50) M^+, 111 (19.5) $C_6H_{11}CO$, 83 (100) cyclohexyl, 59 (35.5) CH_3CH_2CHOH; IR 3320, 1708, 1453, 1417, 1314. Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.59; H, 10.81.

2-Hydroxy-1-(1-methylcyclohexyl)-1-butanone: ^1H NMR δ 4.5 (m, 1 H), 1.95 (m, 3 H), 1.5 (m, 10 H), 1.2 (s, 3 H), 1.0 (t, J = 8.8 Hz, 3 H); ^{13}C NMR δ 218.0, 73.4, 46.7, 34.7, 34.1, 28.1, 25.6, 23.7, 22.5, 22.3, 9.3; MS 184 (0.36) M^+, 125 (3.60) M - C_3H_7O, 97 (100) methylcyclohexyl, 88 (11.14) $CH_3CH_2CH(OH)CHO$; IR 3478, 1698, 1457, 1403, 1378. Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.70; H, 10.94. Found: C, 71.59; H, 10.95.

2-Hydroxy-1-(1-methylcyclohexyl)-2-phenylethanone: ^1H NMR δ 7.35 (m, 5 H), 5.45 (m, 1 H), 4.45 (m, 1 H), 1.4 (m, 10 H), 0.9 (s, 3 H); MS 215 (0.2), 136 (2.6) PhCH(OH)CHO, 125 (13.1) $CH_3C_6H_{10}CO$, 107 (33.4) PhCHOH, 97 (100) methylcyclohexyl, 77 (22.3) Ph. Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.43; H, 8.39.

3-Hydroxy-4-dodecanone: ^1H NMR δ 4.4 (m, 1 H), 4.2 (m, 1 H), 2.5 (m, 2 H), 1.7 (m, 2 H), 1.3 (m, 12 H), 0.95 (m, 6 H); MS 200 (0.89) M^+, 141 (28.98) $C_8H_{17}CO$, 59 (100) CH_3CH_2CHOH; IR 3492, 1715, 1461, 1411. Anal. Calcd for $C_{12}H_{24}O_2$: C, 71.95; H, 12.07. Found: C, 72.16; H, 11.89.

1-(1-Hydroxycyclohexyl)-1-nonanone: ^1H NMR δ 3.6 (m, 1 H), 2.55 (t, J = 8.1 Hz, 2 H), 1.67 (m, 10 H), 1.27 (m, 12 H), 0.88 (t, J = 6.2 Hz, 3 H); ^{13}C NMR δ 214.2, 77.2, 35.0, 33.1, 31.1, 28.7, 28.6, 28.4, 24.6, 23.1, 21.9, 20.4, 13.4; MS 241 (0.63) M^+, 141 (0.45) $C_8H_{17}CO$, 99 (100) $C_6H_{10}OH$, 81 (30.79) cyclohexenyl. Anal. Calcd for $C_{15}H_{28}O_2$: C, 74.95; H, 11.74. Found: C, 75.01; H, 11.48.

1-(1-Hydroxycyclohexyl)ethanone: ^1H NMR δ 3.6 (m, 1 H), 2.25 (s, 3 H), 1.6 (m, 10 H); MS 143 (0.16) M^+, 99 (98) $C_6H_{10}OH$, 81 (100) cyclohexenyl. Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.33; H, 9.96.

Note Added in Proof: We recently found that benzoyl chloride gives **3** mainly when quenching is performed in anaerobic conditions. Benzil **2** has been therefore produced by very fast air oxidation of precursor ene diol prior to tautomerization to **3** (for a similar observation, see: Duhamel, L.; et al. *Tetrahedron Lett.* **1983**, *24*, 4209).

Binding of Dihydroxybenzenes in Synthetic Molecular Clefts

Rint P. Sijbesma and Roeland J. M. Nolte*

Department of Organic Chemistry, University of Nijmegen, Toernooiveld 6525 ED Nijmegen, The Netherlands

Received June 22, 1990

Synthetic molecular clefts of type 1 strongly bind dihydroxybenzenes in organic solvents. The association constants have values up to 3×10^5 M^{-1}. The guests are sandwiched between the *o*-xylylene walls of the host and form hydrogen bonds with the receptor.

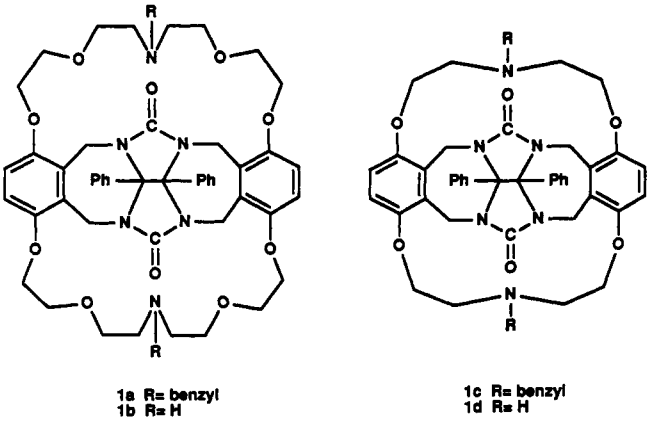
Introduction

In the growing field of host–guest chemistry, much work is currently being directed toward the development of receptors that recognize neutral molecules in aqueous as well as in organic solvents.[1] Recognition is an important step in enzymatic catalysis, in selective transport, and in various other biological processes in living systems. Research on host–guest systems has mostly been focused on two aspects: (i) to gain a better understanding of the intermolecular interactions involved and (ii) to attain the same high selectivity as found in the natural systems.

We are interested in selective synthetic receptors for dihydroxybenzenes (DHB's) as part of our program aimed at the development of a dopamine β-hydroxylase mimic.[2]

In this paper we report on the strong complexation of DHB's in the new synthetic receptors **1a–d**[3] (Chart I).

Chart I

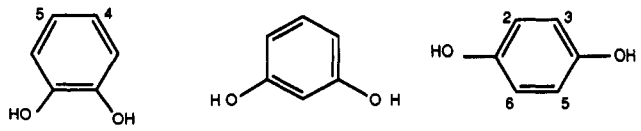


These compounds contain a cleft which is formed by a diphenylglycoluril unit and two *o*-xylylene rings. These

(1) Diederich, F. *Angew. Chem.* **1988**, *100*, 372.
(2) Martens, C. F.; Nolte, R. J. M. To be published.

0022-3263/91/1956-3122$02.50/0

Chart II



Catechol (CAT) Resorcinol (RES) Hydroquinone (HQ)

Table I. Association Constants, Calculated Saturation Shifts of the Probe Signals in the Receptor [$\Delta\delta_{sat}$], and Free Energies of Complexation for Complexes of Receptor 1a with DHB's in $CDCl_3$ at 298 ± 2 K

entry	DHB	$K_a \times 10^{-2}$,[a] M^{-1}	$\Delta\delta_{sat}$, ppm	$-\Delta G°$, kJ mol^{-1}
1	CAT	0.70	0.50	10.5 ± 0.1
2	4,5-Br_2-CAT	12[b]	0.34	17.6 ± 0.2
3	RES	29	0.51	19.7 ± 0.1
4	HQ	6.5	0.64	16.0 ± 0.2
5	2-Cl-HQ	15[b]	0.48	18.0 ± 0.2
6	2-Br-HQ	18	0.48	18.5 ± 0.1
7	2,3-Cl_2-HQ	7.2[b]	0.56	16.3 ± 0.2
8	2,5-Cl_2-HQ	–[c]	–	–
9	2,3-Br_2-HQ	14	0.51	17.9 ± 0.1
10	2,5-Br_2-HQ	–[c]	–	–
11	2,3-CN_2-HQ	3000[d]	0.47	31.2 ± 1.0

[a] Estimated error in K_a 4%, unless otherwise indicated. [b] Estimated error 10%. [c] Induced shifts too low to determine K_a. [d] This value was determined by a solid–liquid ($CDCl_3$) extraction experiment (see Experimental Section), estimated error in K_a 50%.

rings have an almost parallel orientation and a fixed mutual distance (≈6 Å between the centers of the xylylene rings).[4] They are connected by two aza-crown ether bridges. The nitrogen atoms in these bridges are capable of forming hydrogen bonds with the OH groups of the DHB's.

Results and Discussion

Complexation of various DHB's by receptors **1a** and **1b** was investigated with ^1H NMR spectroscopy in $CDCl_3$. Upon titrating the receptor with a DHB, the signals of the cavity wall protons shift upfield. Titrating a DHB with one of the receptors leads to an upfield shift of the DHB aromatic proton signals, whereas the signals of the OH protons shift downward. These shifts indicate that the guest molecules are bound inside the cavities of **1a** and **1b**, with the OH groups forming hydrogen bonds with the receptor. Downfield shifts and a broadening of the signals of the CH_2N protons in the bridges of the receptor suggest that the nitrogen atoms are involved in hydrogen bonding, although hydrogen bonding with the carbonyl groups cannot be excluded, in particular in the case of complexation of resorcinol. Association constants (K_a's) and saturation shift values of the host signals were calculated with the aid of a computer program.[5,6] Excellent fits were obtained assuming that only 1:1 complexation takes place.

Binding constants for **1a** with the three isomeric DHB's (Table I, entries 1, 3, and 4) decrease in the order resorcinol > dihydroquinone > catechol. The low K_a of catechol is probably due to the presence of an intramolecular hydrogen bond in this molecule.[7] In order to form two hydrogen bonds with the receptor, this intramolecular hydrogen bond has to be broken. Consequently, the gain in free energy upon complexation of catechol in **1a** is much lower than upon complexation of the other two DHB's. $\Delta H°$ and $\Delta S°$ values for the formation of the complex of **1a** with catechol were determined by evaluating the binding constants at four different temperatures. These values are $\Delta H° = -22.0 \pm 0.1$ kJ mol^{-1} and $\Delta S° = -36 \pm 3$ J mol^{-1} K^{-1}, suggesting that the complexation is enthalpy driven.

Table II. Association Constants [K_a, M^{-1}] of Complexes between Receptors 1a–d and Dihydroxybenzenes[a]

receptor	CAT	RES	HQ
1a	70[b]	2.9×10^3[b]	6.5×10^2[b]
1b	40	2.0×10^3	5.4×10^3
1c	<50	50	<50
1d	5.0×10^2	3.2×10^3	5.5×10^2

[a] Estimated error 50%, unless otherwise indicated. [b] Estimated error 5–10%, see Table I.

Electron-withdrawing substituents in the guest have a positive effect on the binding. This is apparent when the binding constants of 4,5-dibromocatechol and of 2,3-dicyanodihydroquinone are compared with the binding constants of the parent DHB's (Table I, entries 1, 2, 4 and 11). The OH groups of the DHB's with electron-withdrawing substituents can form stronger hydrogen bonds than those of the unsubstituted DHB's. In case of the complex of **1a** and 2,3-dicyanodihydroquinone this leads to an association constant of 3×10^5 M^{-1}. This is one of the highest binding constants reported for a complex between a synthetic receptor and a neutral guest in an organic solvent.[8]

It is more difficult to explain the differences in K_a values of the halogen-substituted dihydroquinones because several factors influence the binding of these guests. Introduction of a halogen substituent increases the hydrogen-bond acidity of the OH groups, but at the same time OH groups ortho to a halogen substituent become partly intramolecularly hydrogen bonded.[9] If only one halogen substituent is present, the OH group meta to this halogen forms a stronger hydrogen bond with the receptor than the OH group of dihydroquinone itself. The hydrogen bond of the ortho OH group with the receptor will be about as strong as in dihydroquinone, due to the opposing effects of electron withdrawal and intramolecular hydrogen bonding. The net effect of the introduction of one halogen substituent, therefore, is an increase of the association constant. Upon introducing a second halogen atom, both OH groups become intramolecularly hydrogen bonded. For the 2,3-dihalogeno-substituted dihydroquinones, the association constants fall between those of the corresponding monosubstituted dihydroquinones and of dihydroquinone itself. If there are substituents on each side of the dihydroquinone ring (as in 2,5-dichlorodihydroquinone and in 2,5-dibromodihydroquinone), binding is sterically inhibited; the substituents are too large to allow the guest to enter the cavity deeply enough to form two hydrogen bonds with the receptor. With these guests, complexation-induced shifts fall below the limit of detection, and the binding constants for complexation in the cavity are very small. Compound **1a** thus is able to dis-

(3) Other examples of receptors for hydroxybenzenes have been published: (a) Sheridan, R. E.; Whitlock, H. W., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 4071. (b) Watson, W. H.; Vögtle, F.; Müller, W. M. *J. Inclusion Phenom.* **1988**, *6*, 491. (c) Ebmeyer, F.; Vögtle, F. *Angew. Chem.* **1989**, *100*, 95. (d) Hayakawa, K.; Kido, K.; Kanematsu, K. *J. Chem. Soc., Perkin Trans. 1* **1988**, 511.

(4) Smeets, J. W. H.; Sijbesma, R. P.; van Dalen, L.; Spek, A. L.; Smeets, W. J. J.; Nolte, R. J. M. *J. Org. Chem.* **1989**, *54*, 3710.

(5) de Boer, J. A. A.; Reinhoudt, D. N.; Harkema, S.; van Hummel, G. J.; de Jong, F. *J. Am. Chem. Soc.* **1982**, *104*, 4073.

(6) Granot, J. *J. Magn. Reson.* **1983**, *55*, 216.

(7) Spencer, J. N.; Heckmann, R. A.; Harner, R. S.; Shoop, S. L.; Robertson, K. S. *J. Phys. Chem.* **1973**, *77*, 3103.

(8) A K_a of 1.0×10^6 has been reported for a complex between a synthetic receptor and uric acid: Kelly, T. R.; Maguire, M. P. *J. Am. Chem. Soc.* **1987**, *109*, 6549.

(9) Baker, A. W. *J. Am. Chem. Soc.* **1958**, *80*, 3598.

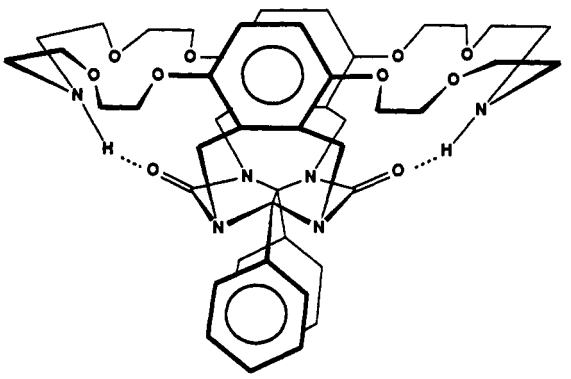


Figure 1. Side view of receptor **1b**.

criminate strongly between isomeric DHB's (Table I, entries 7–10).

In Table II the complexation properties of the four receptors **1a–d** for catechol, resorcinol, and dihydroquinone are compared. Receptor **1b** binds dihydroquinone much more strongly than **1a**, while binding of resorcinol and catechol is weaker. This altered preference is probably caused by the presence of intramolecular hydrogen bonds between the NH groups and the urea carbonyl groups in receptor **1b**.[10] CPK models suggest that these hydrogen bonds keep the nitrogen atoms at a fixed position, with their free electron pairs pointing into the cavity (Figure 1). The distance between these electron pairs is ideally suited for making two hydrogen bonds with dihydroquinone. The stronger binding of dihydroquinone by **1b** than by **1a** is an example of Cram's "principle of preorganisation",[11] which states that hosts having low conformational freedom lose less entropy upon complexation of a guest, and hence bind stronger and more selectively.

Receptors **1c** and **1d** were designed to achieve selective binding of catechol and catechol derivatives such as dopamine. In **1c** and **1d** the nitrogen atoms in the bridges are at the appropriate distance to form two hydrogen bonds with the catechol OH groups. Because the DHB's cannot enter the cavities of **1c** and **1d** sufficiently deeply, the complexation-induced shifts are rather low. Therefore, the binding constants of these receptors were determined by means of competition experiments with host **1a**. For reasons that are not yet clear to us, host **1c** binds all investigated DHB's very weakly. Receptor **1d**, however, is a much better binder of catechol than hosts **1a** and **1b**. When going from **1b** to **1d** the association constant increases by a factor of 12.5. For resorcinol this increase is only by a factor of 1.6, whereas for dihydroquinone even a 10-fold decrease in binding constant is observed. With 4,5-dibromocatechol, **1d** forms a 1:1 complex that precipitates from solution.

In summary, our experiments indicate that receptor molecules **1** display strong binding properties for dihydroxybenzenes. Furthermore, we have shown that it is possible to tune the binding preference of these receptors by altering the geometry of the binding sites.

Experimental Section

Compounds **1a–d** were synthesized according to procedures described previously by us.[4] The physical properties of **1a** and **1b** have been published.[4] Those of **1c** and **1d** are as follows:

1,6:3,4-Bis[3,3′:6,6′-bis(4-aza-4-benzyl-1,7-dioxaheptamethylene)-1,2-xylylene]tetrahydro-3a,6a-diphenylimidazo-[4,5-*d*]imidazole-2,5(1*H*,3*H*)-dione (1c). This compound was purified by column chromatography (silica gel, eluent $CHCl_3$/MeOH): yield 73%; mp >200 °C dec; IR (KBr) 3080–2980 (ArH), 1705 (C=O), 1150–1050 (COC); ^{1}H NMR ($CDCl_3$) δ 7.40 (m, 10 H, ArH), 7.11 (m, 10 H, ArH), 6.84 (s, 4 H, ArH), 5.45 and 3.65 (2 d, 8 H, NCH_2Ar, J = 15.4 Hz), 3.70 (m, 12 H, OCH_2CH_2, NCH_2Ar), 3.45 and 3.02 (m, 8 H, NCH_2CH_2); FAB-MS (*m*-nitrobenzyl alcohol) m/z 881 $(M + H)^+$. Anal. Calcd for $C_{54}H_{52}N_6O_6 \cdot H_2O$: C, 72.14; H, 6.05; N, 9.35. Found: C, 72.62; H, 5.95; N, 9.34.

1,6:3,4-Bis[3,3′:6,6′-bis(4-aza-1,7-dioxaheptamethylene)-1,2-xylylene]tetrahydro-3a,6a-diphenylimidazo[4,5-*d*]-imidazole-2,5(1*H*,3*H*)-dione (1d). This compound was purified by column chromatography (silica gel, eluent $CHCl_3$/MeOH/Et_3N): yield 95%; mp >200 °C dec; IR (KBr) 3310 (NH), 1705 (C=O), 1150–1050 (COC); ^{1}H NMR ($CDCl_3$) δ 7.10–7.17 (m, 10 H, ArH), 6.62 (s, 4 H, ArH), 5.50 and 3.65 (2 d, 8 H, NCH_2Ar, J = 15.4 Hz), 4.31 and 4.23 (2 m, 8 H, OCH_2CH_2), 3.05 and 2.93 (2 m, 8 H, NCH_2CH_2), 2.40 (s, 2 H, NH); FAB-MS (*m*-nitrobenzyl alcohol) m/z 701 $(M + H)^+$.

Dihydroxybenzenes. Dihydroquinone, catechol, resorcinol, and 2,3-dicyanodihydroquinone were commercial products. Brominated dihydroquinones were obtained by reaction of dihydroquinone with bromine in CCl_4 and separation of the products by careful column chromatography with EtOAc/*n*-hexane as eluent. Chlorinated dihydroquinones were obtained by reaction of dihydroquinone with SO_2Cl_2 in diethyl ether.[14] The products were separated by column chromatography ($CHCl_3$/MeOH). 4,5-Dibromocatechol was prepared by bromination of catechol with bromine in $CHCl_3$. All dihydroxybenzenes were further purified by repeated recrystallization or sublimation at reduced pressure. Purity was checked by comparison of the melting points with literature values.[14,15]

^{1}H NMR Titrations. The protocol of Granot was followed so far as compound solubility and spectrometer sensitivity allowed.[6] Each titration was carried out with 10 different samples. These samples were prepared from stock solutions of the receptor and the substrate in $CDCl_3$. The concentration of the component of which the ^{1}H NMR signal was monitored was roughly kept constant. The amount of the other component was varied from 0 to 8 equiv. $CDCl_3$ was added to adjust the total volume of each sample to approximately 0.6 mL. Errors in association constants were evaluated from the difference between K_a values in independent titrations and the average K_a values, as well as from the confidence limits on single determinations found with the curve-fitting routine.[12]

Association constants of **1c** and **1d** were determined from competition experiments with **1a**. To a solution of **1a** and a DHB one of these hosts was added and the shifts of the signals of **1a** were monitored.

Due to the insolubility of 2,3-dicyanodihydroquinone in $CDCl_3$, the association constant for the complex between this guest and **1a** was determined by a solid–liquid ($CDCl_3$) extraction experiment conform the literature.[13] In order to estimate the reliability of this procedure, a similar solid–liquid extraction was also carried out with dihydroquinone. This experiment gave a K_a of 1.2×10^3 M^{-1} which is in the same range as the value found with the titration method (6.5×10^2 M^{-1}, see Table I). As a further check the K_a values of dihydroquinone and 2,3-dicyanodihydroquinone were also determined by ^{1}H NMR titrations in a solvent mixture in which both guests are soluble, viz. $CDCl_3$/acetonitrile, 4:1, v/v. These values are 12 M^{-1} and 4.2×10^3 M^{-1}, respectively. Assuming the ratio of association constants to be independent of solvent, one calculates a value of 2.3×10^5 M^{-1} for the K_a of **1a** with dicyanodihydroquinone in $CDCl_3$. This value is very similar to the one obtained by the solid liquid extraction method ($K_a = 3 \times 10^5$, Table I).

(10) The NH proton in **1b** has a sharp resonance at 4.70 ppm. NH protons of other secondary amines display broad resonances at ≈2 ppm.
(11) Cram, D. J. *Angew. Chem.* **1986**, *98*, 1041.
(12) Press, W. H.; Flannery, B. P.; Teukolsky, S. A.; Vetterling, W. T. *Numerical Recipes*; Cambridge University Press: Cambridge, 1986.
(13) Diederich, F.; Dick, K. *J. Am. Chem. Soc.* **1984**, *106*, 8024.
(14) Ter Borg, A. P. *Recl. Trav. Chim. Pays-Bas* **1954**, *73*, 5.
(15) (a) Norris, R. K.; Sternhell, S. *Aust. J. Chem.* **1973**, *26*, 333. (b) Biilmann, E.; Jensen, A. L.; Pedersen, K. O. *J. Chem. Soc.* **1925**, *127*, 205. (c) Kohn, M. *J. Am. Chem. Soc.* **1950**, *73*, 480.