Influence of Highly Preorganised 7,7-Diphenylnorbornane in the Free Energy of Edge-to-Face Aromatic Interactions

Antonio García Martínez,* José Osío Barcina,* and Álvaro de Fresno Cerezo[a]

Abstract: The influence of preorganised 7,7-diphenylnorbornane in the stability (K_a) of host–guest complexes as well as in the determination of the energy of edge-to-face aromatic interactions has been investigated. The guest molecules studied bind more strongly with hosts that contain the cofacial 7,7-diphenylnorbornane subunit than with similar hosts that have a 1,1-diphenylcyclohexane subunit. On the other hand, the value of the edge-to-face aromatic interactions calculated for our complexes (-0.2 ± 0.6 kJ mol^{-1}) is significantly lower (by a factor of seven) than the one previously reported in the literature. This result highlights the importance of entropic factors in the determination of weak noncovalent interactions.

Keywords: aromatic interactions · diphenylnorbornane · host–guest chemistry · noncovalent interactions

Introduction

Although noncovalent interactions have been known for more than a century,[1] it is mainly during the last decades that the essential role they play in biology, chemistry and materials science has been shown.[2, 3] Despite their importance, the study of these weak interactions is not always easy[4] because frequently they act simultaneously or are masked by other interactions, especially in biological systems. Therefore, the design of adequate models for the study of a particular interaction is an important tool in chemistry and, in some cases, remains a challenge.

An interesting approach to the quantification of aromatic edge-to-face interactions[6] by using chemical double-mutant cycles (a combination of thermodynamic cycles and mutagenesis) has recently been proposed.[5] In this approach, a value of -1.4 ± 0.8 kJ mol^{-1} for the aromatic edge-to-face interaction was obtained by comparing the stabilities (ΔG) of complexes **A**–**D** (Scheme 1). The accuracy of this methodology is based on the assumption that both the host and the guest are essentially rigid; therefore, "the experiments are not complicated by losses of conformational mobility on complexation" and, as a consequence, the geometry of the interactions is almost the same in each complex.[5] However, this argument has received some criticism[7] on the basis that the models in Scheme 1 are not in fact rigid because of the rotatable benzylic bonds. This fact makes entropic contributions non-negligible because conformations may be different in each complex.[7] On the other hand, the structural determination of supramolecular aggregates remains a major problem, particularly in the case of weakly bonded complexes. Thus, there is some doubt about the face-to-face or propeller-like conformation of the aryl groups of the 1,1-diphenylcyclohexane subunit in the supramolecular-zipper systems **A**–**D**.[5]

[a] Dr. J. Osío Barcina, Prof. Dr. A. García Martínez, Dr. Á. de Fresno Cerezo
Departamento de Química Orgánica
Facultad de Ciencias Químicas
Universidad Complutense
Ciudad Universitaria, 28040 Madrid (Spain)
Fax: (+34) 91-3944103
E-mail: josio@eucmos.sim.ucm.es

Results and Discussion

As can be seen in Scheme 1, the main nucleus of the host molecules in complexes **A**–**D** is a subunit of 1,1-diphenylcyclohexane (DPC; **1**). In our opinion, the lack of conformational stability in this subunit of the complexes could also affect the determination of the free energy of complexation of compounds **3b** and **3c**. Diphenylmethane (DPM) and some of its derivatives are frequently used in the construction of macrocycles,[8] catenanes,[9] rotaxanes[9a, 10] and other host molecules.[11] This subunit provides an electron-rich zone able to facilitate the complexation of the guest, especially in neutral hosts;[8d–j, m, 11e] the face-to-face arrangement being the optimal conformation for the formation of host–guest complexes in most cases. However, the DPC subunit is far from being rigid, even when placed in the structure of macrocycles. Surprisingly, no thermodynamic study of the conformations of DPC has been carried out until now. Only calculations of the potential energy surface (PES) of the parent compound, DPM, have been published.[12] A rotational barrier of about 2.7 kJ mol^{-1} has been determined for DPM and its more stable

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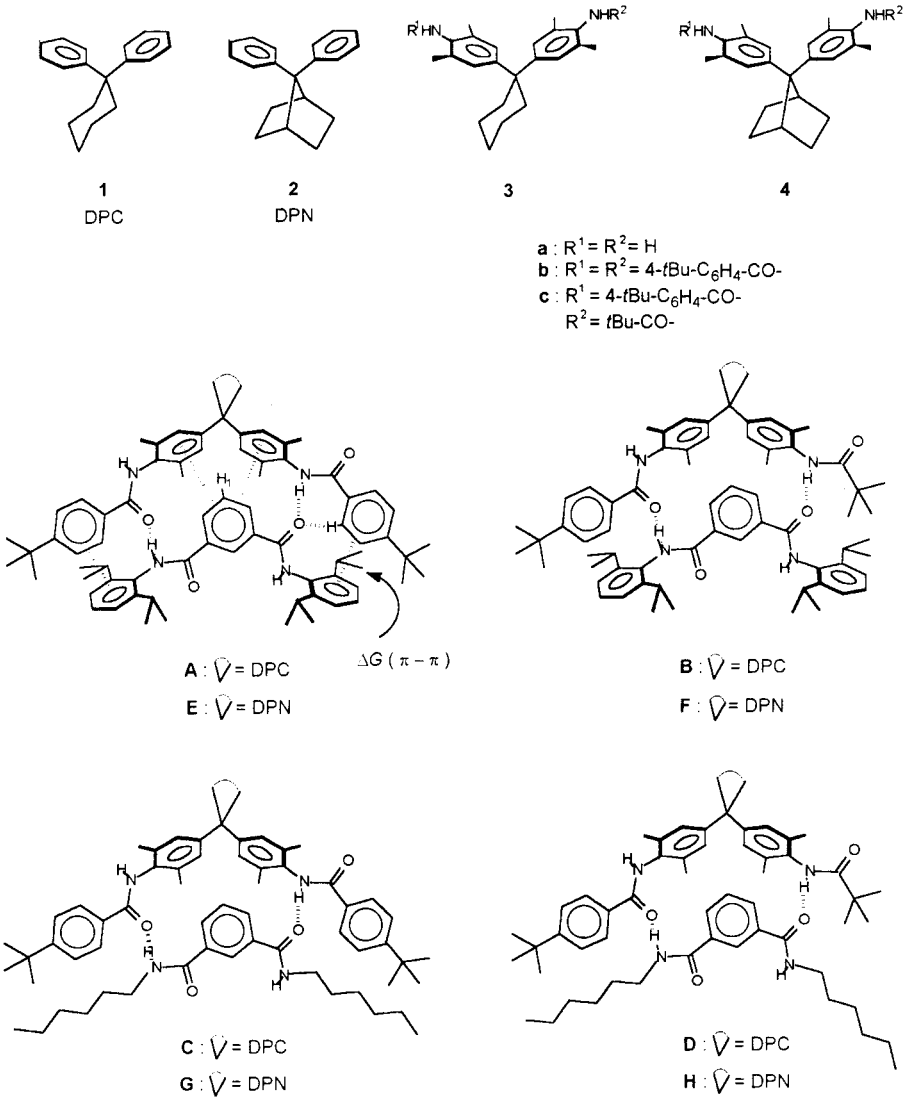


Scheme 1. Structures of DPC, DPN and complexes **A**–**H**.

conformation has the aryl groups arranged in a propeller-like conformation (C_2 symmetry, torsional angle 57.0° according to the B3LYP/6-31G* method[12b]). This situation has prompted us to undertake the calculation of the free energy surface (FES) of DPC by using the ab initio RHF/STO-3G method.[13] The energies and free energies (at 20 °C) of the cofacial, propeller and perpendicular conformations are given in Table 1. The global minimum corresponds to the propeller conformation **1b**, with C_{ipso}-C-$C_{ipso'}$-C_{ortho} torsional angles of −58.1° and −71.7°. The perpendicular **1c** and cofacial **1a** conformations are first-order saddle points (an imaginary frequency was found for both conformations). The global maximum is the cofacial conformation **1a**.

We have previously shown[14] that 7,7-diphenylnorbornane (DPN; **2**; Scheme 1) is a highly preorganised diphenylmethane derivative in which, due to the steric hindrance of the exo-H of the norbornane framework, the most stable conformation has the aryl rings in an apical face-to-face arrangement with C_{2v} symmetry. As a consequence, a new homoconjugative band is observed in the UV spectrum. This substrate has been used to study the nature of aromatic face-to-face interactions,[15] in the synthesis of homoconjugated polymers[16] and in the preparation of new homoconjugated chromophores with nonlinear optic (NLO) properties.[17]

In view of the above, we decided to reinvestigate the quantification of the aromatic edge-to-face interaction by using host molecules in which DPC was replaced by DPN (complexes **E**–**H**, Scheme 1). In our opinion, this change should contribute to the study of the entropic contributions that affect the measurement of the edge-to-face interactions. The results of our study are summarised in Table 2, together with literature values for the related complexes **A**–**D**. The values in Table 2 were determined by assuming a 1:1 stoichiometry in the formation of complexes **E**–**H**[18] and that association (dimerisation) of the components is negligible. Association constants (K_a) were determined by using the Benesi–Hildebrand equation.[18, 19]

At first sight, the data reported in Table 2 show that the association constants (K_a) in the complexes with a DPC subunit (**A**–**D**) are very similar to those with a DPN (**E**–**H**) subunit. However, a more detailed analysis reveals some important differences. We measured the association constant of complex **A** and obtained a value of $31 \pm 2\,M^{-1}$, which is significantly lower than the one reported in the literature ($48 \pm 2\,M^{-1}$).[5] Therefore, complex **E**

Table 1. Energies (E) and free energies (G) (no scaled values) of the cofacial (point group C_s), propeller (C_1) and perpendicular (C_s) conformations of DFC calculated with the ab initio RHF/STO-3G method.

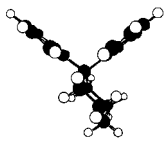
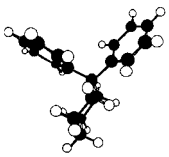
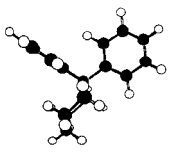
	 **1a**, C_s	 **1b**, C_1	 **1c**, C_s
E [kJ mol^{-1}]	−1798374.1	−1798379.4	−1798376.7
G [kJ mol^{-1}]	−1797451.7	−1797459.5	−1797458.4

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Table 2. Association constants (K_a) [mol^{-1}] and free energies (ΔG) [$kJ\,mol^{-1}$] of complexes **A**–**H** and value of the chemical shift of the pure complex relative to the shift of the pure guest in solution (Δ_o) for the isophthaloyl proton H1.

Complex	K_a	ΔG(I)	Δ_o	Complex	K_a	ΔG(II)	$\Delta\Delta G$[a]
E	48 ± 3	-9.5 ± 0.2	-1.95	**A**	48 ± 2[b]	-9.6 ± 0.1	$-0.1(1.2)$[c]
F	25 ± 2	-7.8 ± 0.2	-2.01	**B**	17 ± 2[b]	-7.1 ± 0.3	0.7
G	20 ± 2	-7.3 ± 0.3	-0.66	**C**	15 ± 3[b]	-6.8 ± 0.5	0.5
H	11 ± 2	-5.8 ± 0.5	0.97	**D**	10 ± 2[b]	-5.7 ± 0.5	0.1
A	31 ± 2	-8.3 ± 0.2	-1.75				

[a] $\Delta\Delta G = \Delta G(\text{II}) - \Delta G(\text{I})$. [b] Ref. [5]. [c] Calculated from the ΔG(I) value obtained in this work for complex **A**.

has a higher K_a than **A** or, in other words, the guest molecule binds more strongly to a host possessing a DPN subunit that is preorganised with the aryl groups in a face-to-face conformation.

Some interesting conclusions about the structure of the complexes can be reached from the energy data obtained from thermochemical calculations. As can be seen (Table 1), the energy difference (ΔE) between the more stable propeller (**1b**) and the cofacial (**1c**) conformations of DPC is 5.3 $kJ\,mol^{-1}$. On the other hand, by considering the difference between rotational and vibrational entropies of the whole molecule, an intrinsic ΔG value of 7.8 $kJ\,mol^{-1}$ (at 20 °C) is obtained for the formation of complexes in a cofacial configuration (in relation to the propeller conformation) from the isolated molecules of DPC (Table 1). Besides this, the fact that the propeller–cofacial change causes a decrease in the entropy of mixing of Rln2 should be considered.[20] This represents an increase of free energy of 1.7 $kJ\,mol^{-1}$ at 20 °C. Therefore, the formation of a complex with the DPC subunit in a cofacial conformation requires an increase of free energy (ΔG) of 9.5 $kJ\,mol^{-1}$ in comparison with the propeller conformation. In the case of complexes from the substituted DPC subunit, **3b** and **3c** (Scheme 1), this ΔG value should be even higher because, due to the electrostatic repulsion between the electron-rich aryl rings in the cofacial disposition, ΔE is expected to be higher.[15] It can be concluded that cofacial supramolecular complexes derived from the DPN subunit **4b** or **4c** (Scheme 1) should be more stable (by ca. 9.5 $kJ\,mol^{-1}$) than complexes derived from **3b** or **3c**. However, this assumption is not in agreement with the experimental results (Table 2). As can be seen, the free energy difference between complexes **A** and **E** is only 1.2 $kJ\,mol^{-1}$ (from our results). This discrepancy clearly shows that the aryl rings of **3b** and **3c** are not arranged in a cofacial conformation in their complexes[21] and seems to indicate that in complexes **A**–**D** this subunit is almost in the propeller C_1 conformation, depicted in Table 1, but with hindered racemisation (libration) due to the interactions between the ring of the isophthaloyl moiety and the aryl rings of **3b**/**3c**. Moreover, the difference between the free energy of complexes **E**–**H** and the free energy of complexes **A**–**D** reported in the literature[5a] ($\Delta\Delta G$; Table 2), varies from -0.1 to 0.7. If the geometry of the central nucleus of complexes **A**–**D** were be the same as in complexes **E**–**H**, the value of $\Delta\Delta G$ should be constant. The variations observed can be explained by considering that the conformation of subunit **3b**/**3c** in complexes **A**–**D** is not the same in each case. On going from complex **B** to complex **D** the value of $\Delta\Delta G$ decreases with the stability of the complexes; this shows that the edge-to-face interactions between the three central aryl rings are not constant. Thus, as a result of the decrease of the central edge-to-face interaction, there is an increase in the mobility of the aryl rings of **3b** and **3c** and, therefore, in the racemisation rate of the complexes; while in **E**–**H**, the DFN subunit is fixed in a cofacial conformation.

The difference in stability between the two complexes **A** and **E** is also revealed by the differences in complexation-induced changes in the ^{1}H NMR chemical shift (Figure 1). As

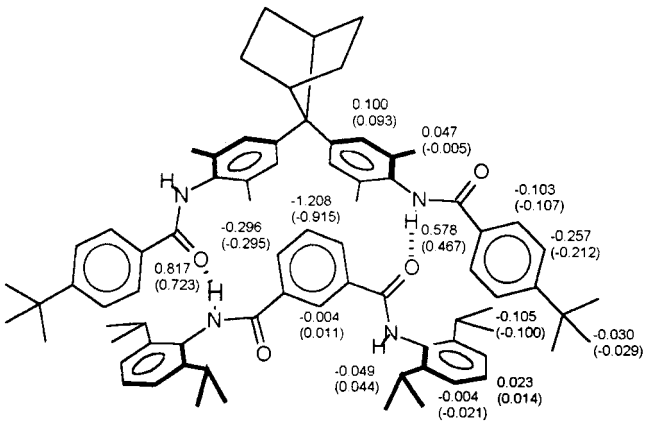

Figure 1. Complexation-induced changes in ^{1}H NMR ($CDCl_3$) shifts of complexes **E** and **A** (in brackets).

can be seen, the values of the induced changes in chemical shifts (measured at the same concentration) in complex **E** are more pronounced than in complex **A** (in brackets) due to the fact that in complex **A** the aromatic pocket of the host is arranged in a propeller conformation. As a result of this, the geometry of the complexes is different, with the distance between the host and the guest probably larger in the case of **A** than in **E** because of a weaker binding complexation. A relevant argument in favour of this assumption is that the highest differences in the complexation-induced changes in chemical shifts are observed in the aromatic proton of the isophthaloyl group of the guest, which lies directly in the aromatic pocket of the host, and the protons involved in the hydrogen bonds, the main forces stabilising the complexes.

The question now is what influence the use of complexes **E**–**H** (with higher preorganisation and K_a) may have on the determination of the edge-to-face interaction between the terminal rings of complexes **A** and **E**. The magnitude of this interaction is given by the equation: $(\Delta G_A - \Delta G_B) - (\Delta G_C - \Delta G_D)$. According to this, a value of -0.2 ± 0.6 $kJ\,mol^{-1}$ for the aromatic edge-to-face interaction is obtained from our ΔG values; this is considerably lower (by a factor of 7) than the result reported previously with complexes **A**–**D** (-1.4 ± 0.8 $kJ\,mol^{-1}$).[5] Moreover, in complexes **E**–**H** the interaction between the C–H bonds of the terminal aryl rings of the host and the C=O carbonyl amide of the guest, whose value is given by $\Delta G_C - \Delta G_D$ (Scheme 1), is stronger (-1.5 ± 0.8 $kJ\,mol^{-1}$) than the aromatic edge-to-face interaction. In

complexes **A**–**D**, the opposite relationship (-1.1 kJ mol^{-1} versus -1.4 kJ mol^{-1}) is obtained.[5] On the other hand, ΔG_D reflects the sum of the values of the amide hydrogen bonds and two edge-to-face aromatic interactions. Assuming that the contribution of these aromatic interactions is small, the resulting energy of the amide hydrogen bond, which is nearly the same in both complexes **D** and **H** ($\approx -2.7 \pm 0.3$ kJ mol^{-1}), is lower than the average value reported for the amide hydrogen bond,[7a] probably because the geometry of the hydrogen bonds in these complexes is not optimal,[7a,b, 22] due to steric hindrance.

Finally, an important factor that could have an influence on the determination of the aromatic edge-to-face interaction by using these models is the variation in the geometry of the complexes introduced by changes in the substitution of the host and guest molecules. Although X-ray data are not available,[21] the value of the chemical shift of the pure complex relative to the shift of the pure guest in solution (Δ_o), calculated with the Benesi–Hildebrand equation,[19] can give some valuable information. In Table 2 the corresponding values for proton H1 of the guest (Scheme 1) are reported. As can be seen, the differences found in the four complexes **E**–**H** are rather high and difficult to explain only by means of substituent changes; this points to some differences in the geometry of the complexes, although it should be remembered that small changes in the geometry cause large variations in the complexation-induced changes in chemical shifts, due to the anisotropy of the aromatic rings.[21]

Conclusion

In this work we have reinvestigated the determination of aromatic edge-to-face interactions through chemical double-mutant cycles using more preorganised complexes; they were made by changing the 1,1-diphenylcyclohexane (DPC; **1**) subunit of the hosts to the cofacial 7,7-diphenylnorbornane (DPN; **2**). With this modification, the guest molecules fit into the cavity of the host better and the resulting complexes show higher association constants, mainly due to the lower entropic cost of the complexation.[23] The magnitude of the aromatic edge-to-face interaction between the terminal aryl groups calculated by us with complexes **E**–**H** is small (-0.2 ± 0.6 kJ mol^{-1}) and lower (by a factor of seven) than the result reported in the literature obtained with diphenylcyclohexane-derived host molecules. These results suggest, in agreement with previous opinions,[7a] that the lack of rigidity of the molecules chosen as models for this study is an important limitation in the accurate determination of weak interactions, since a small change in the structure of the model leads to considerably different results. Finally, as we mentioned in the introduction, diphenylmethane derivatives are frequently used in the construction of supramolecular structures. In our opinion, 7,7-diphenylnorbornane (**2**) can advantageously be used instead of other diphenylmethane derivatives in situations in which a high preorganisation is required. Further work on the use of 7,7-diphenylnorbornane in the design of host molecules is currently under way.

Experimental Section

All compounds in this work have been prepared according to procedures described earlier.[5, 9b, 24]

Compound 4a: M.p. 283.0–285.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 6.93$ (s, 4H), 3.20 (s, 4H), 2.98–2.90 (m, 2H), 2.11 (s, 12H), 1.70–1.50 (m, 4H), 1.30–1.10 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 139.7, 136.6, 126.9, 121.5, 62.9, 41.7, 28.7, 17.9$; MS (60 eV, EI): *m*/*z* (%): 334 (55) $[M]^+$, 320 (21), 319 (100), 253 (31), 198 (18), 159 (21), 134 (45), 131 (60), 124 (50), 116 (26).

Compound 4b: M.p. 227.3–229.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.80$ (d, J(H,H) = 8.4 Hz, 4H), 7.48 (d, J(H,H) = 8.4 Hz, 4H), 7.35 (s, 2NH), 7.11 (s, 4H), 3.05–2.97 (m, 2H), 2.15 (s, 12H), 1.75–1.60 (m, 4H), 1.35 (s, 18H), 1.40–1.20 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 165.8, 155.0, 144.7, 135.2, 131.8, 131.3, 127.0, 127.0, 125.5, 64.1, 41.5, 34.9, 31.1, 28.4, 18.7$; MS (60 eV, EI): *m*/*z* (%): 655 (8) $[M+1]^+$, 654 (18) $[M]^+$, 161 (100); IR ($CHCl_3$): $\delta = 3429$ (m), 3155 (m), 1668 (s) cm^{-1}.

Compound 4c: M.p. 206.0–209.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.81$ (d, J(H,H) = 8.3 Hz, 2H,), 7.48 (d, J(H,H) = 8.3 Hz, 2H,), 7.33 (s, NH), 7.09 (s, 2H), 7.07 (s, 2H), 6.82 (s, NH), 3.05–2.95 (m, 2H), 2.15 (s, 6H), 2.11 (s, 6H), 1.72–1.58 (m, 4H), 1.35 (s, 9H), 1.28 (s, 9H), 1.40–1.20 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 176.6, 165.7, 155.1, 144.7, 144.6, 135.1, 135.0, 131.7, 131.3, 131.2, 127.0, 127.0, 127.0, 125.5, 64.0, 41.6, 39.1, 34.9, 31.1, 28.4, 27.7, 18.9, 18.7$; MS (60 eV, EI): *m*/*z* (%): 579 (37) $[M+1]^+$, 578 (79) $[M]^+$, 563 (26), 502 (29), 402 (24), 161 (100), 57 (95); IR ($CHCl_3$): $\delta = 3438$ (w), 3155 (w), 1668 (s) cm^{-1}.

Determination of association constants: K_a values were determined in $CDCl_3$ by means of ^{1}H NMR titrations and by using the Benesi–Hildebrand equation:[19]

$1/\Delta = 1/K_a\, 1/\Delta_o 1/a_o + 1/\Delta_o$

in which Δ is the observed shift of the host (guest) protons for the system in equilibrium relative to the shift for the pure host (guest) in solution; Δ_o is the shift for the host (guest) in the pure complex relative to the shift of the pure host (guest) in solution; a_o is the guest (host) concentration; K_a is the equilibrium constant. The values of K_a and Δ_o were obtained from linear regression analysis, by plotting $1/\Delta$ against $1/a_o$. The concentration of the host was kept constant while the concentration of the guest was varied from a ratio of 1:2 to 1:10 . To determine the error of the measurements, at least three different experiments were carried out and the shifts of 3–4 protons were considered. A second set of experiments in which the concentration of the guest remained fixed and the concentration of the host varied was also carried out. The same conclusions were reached in this case, but due to limited solubility of the host at high a_o values, the accuracy of this determination was considered to be lower and, therefore, these results are not included in Table 2.

Acknowledgements

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[1] J. D. van der Waals, Doctoral Thesis, University of Leiden, **1873**.
[2] K. Müller-Dethlefs, P. Hobza, *Chem. Rev.* **2000**, *100*, 143–167.
[3] a) J.-M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, **1995**; b) F. Vögtle, *Supramolecular Chemistry*, Wiley, Chichester, **1991**.
[4] For discussions about the determination of noncovalent interactions in host–guest complexes, see: a) H.-J. Schneider, *Chem. Soc. Rev.* **1994**, *22*, 227–234; b) H.-J. Schneider, T. Schiestel, P. Zimmerman, *J. Am. Chem. Soc.* **1992**, *114*, 7698–7703; c) H.-J. Schneider, *Angew. Chem.* **1991**, *103*, 1419–1439; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1417–1436.
[5] a) H. Adams, F. J. Carver, C. A. Hunter, J. C. Morales, E. M. Seward, *Angew. Chem.* **1996**, *108*, 1628–1631; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1542–1544; b) H. Adams, K. D. M. Harris, G. A. Hembury, C. A. Hunter, D. Livingstone, J. F. McCabe, *Chem. Commun.* **1996**, 2531–2532; c) F. J. Carver, C. A. Hunter, E. M. Seward, *Chem. Commun.* **1998**, 775–776.

0947-6539/01/0706-1174 $ 17.50+.50/0 *Chem. Eur. J.* **2001**, *7*, No. 6

[6] a) K. Nakamura, K. N. Houk, *Org. Lett.* **1999**, *1*, 2049–2051; b) E. Kim, S. Paliwal, C. S. Wilcox, *J. Am. Chem. Soc.* **1998**, *120*, 11192–11193; c) S. V. Lindeman, D. Kosynkin, J. K. Kochi, *J. Am. Chem. Soc.* **1998**, *120*, 13268–13269, and references therein. See also: d) C. Chipot, R. Jaffe, B. Maigret, D. A. Pearlman, P. A. Kollman, *J. Am. Chem. Soc.* **1996**, *118*, 11217–11224; e) C. A. Hunter, *Chem. Soc. Rev.* **1994**, *22*, 101–109; see also refs [8i, m, 11d].

[7] a) H.-J. Schneider, *Angew. Chem.* **1997**, *109*, 1116–1117; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1072–1073; b) C. A. Hunter, *Angew. Chem.* **1997**, *109*, 1117; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1073.

[8] a) H.-F. Grützmacher, A. Mehdizadeh, A. Mülverstedt, *Chem. Ber.* **1994**, *127*, 1163–1166; b) H.-J. Schneider, T. Blatter, *Angew. Chem.* **1992**, *104*, 1244–1246; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1207–1208; c) C. S. Wilcox, M. D. Cowart, *Tetrahedron Lett.* **1986** 5563–5566; d) S. Apel, M. Czugler, V. J. Griffith, L. R. Nassimbeni, E. Weber, *J. Chem. Soc. Perkin Trans. 2* **1997**, 1949–1953; e) M. B. Inoue, E. F. Velazquez, M. Inoue, Q. Fernando, *J. Chem. Soc. Perkin Trans. 2* **1997**, 2113–2118; f) A. Cattani, A. D. Cort, L. Mandolini, *J. Org. Chem.* **1995**, *60*, 8313–8314; g) D. Parker, M. Rosser, *J. Chem. Soc. Perkin Trans. 2* **1995**, 85–89; h) J. Ratilainen, K. Airola, M. Nieger, M. Böhme, J. Huuskonen, K. Rissanen, *Chem. Eur. J.* **1997**, 3, 749–754; i) C. A. Hunter, *J. Chem. Soc. Chem. Commun.* **1991**, 749–751; j) J. C. Ma, D. A. Dougherty, *Chem. Rev.* **1997**, *97*, 1303–1324; k) M. Herm, T. Schrader, *Chem. Eur. J.* **2000**, *6*, 47–53; l) F. S. McQuillan, H. Chen, T. A. Hamor, C. J. Jones, H. A. Hones, R. P. Sidebotham, *Inorg. Chem.* **1999**, *38*, 1555–1562; m) H. Adams, F. J. Carver, C. A. Hunter, N. J. Osborne, *Chem. Commun.* **1996**, 2529–2530.

[9] a) R. Jäfer, F. Vögtle, *Angew. Chem.* **1997**, *109*, 966–980; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 930–944; b) C. A. Hunter, *J. Am. Chem. Soc.* **1992**, *114*, 5303–5311; c) F. Vögtle, S. Meier, R. Hoss, *Angew. Chem.* **1992**, *104*, 1628–1631; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1619–1622; d) S. Ottens-Hildebrandt, S. Meier, W. Schmidt, F. Vögtle, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1767–1770; e) C. P. McArdle, M. J. Irwin, M. C. Jennings, R. J. Puddephatt, *Angew. Chem.* **1999**, *111*, 3571–3573; *Angew. Chem. Int. Ed.* **1999**, *38*, 3376–3378.

[10] a) R. Schmieder, G. Hübner, C. Seel, F. Vögtle, *Angew. Chem.* **1999**, *111*, 3741–3743; *Angew. Chem. Int. Ed.* **1999**, *38*, 3528–3530; b) C. Seel, F. Vögtle, *Chem. Eur. J.* **2000**, *6*, 21–24; c) C. Seel, A. H. Parham, O. Safarowsky, G. M. Hübner, F. Vögtle, *J. Org. Chem.* **1999**, *64*, 7236–7242; d) G. M. Hübner, J. Gläser, C. Seel, F. Vögtle, *Angew. Chem.* **1999**, *111*, 395–398; *Angew. Chem. Int. Ed.* **1999**, *38*, 383–386; e) A. H. Parham, B. Windisch, F. Vögtle, *Eur. J. Org. Chem.* **1999**, 1233–1238; f) T. Dünnwald, A. H. Parham, F. Vögtle, Synthesis **1998**, 339–348; g) S. Anderson, R. T. Aplin, T. D. W. Claridge, T. Goodson III, A. C. Maciel, G. Rumbles, J. F. Ryan, H. L. Anderson, *J. Chem. Soc. Perkin Trans. 1* **1998**, 2383–2397; h) S. Anderson, T. D. W. Claridge, H. L. Anderson, *Angew. Chem.* **1997**, *109*, 1367–1370; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1310–1313.

[11] a) H.-J. Schneider, T. Blatter, P. Zimmerman, *Angew. Chem.* **1990**, *102*, 1194–1195; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1161–1162; b) H.-J. Schneider, D. Ruf, *Angew. Chem.* **1990**, *109*, 1192-1194; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1159–1160; c) M. R. Caira, A. Horne, L. R. Nassimbeni, K. Okuda, F. Toda, *J. Chem. Soc. Perkin Trans. 2* **1995**, 1063–1067; d) A. P. Bisson, F. J. Carver, C. A. Hunter, J. P. Waltho, *J. Am. Chem. Soc.* **1994**, *116*, 10292–10293; e) L. R. Hanton, C. A. Hunter, D. H. Purvis, *J. Chem. Soc. Chem. Commun.* **1992**, 1134–1136.

[12] a) T. Strassner, *Can. J. Chem.* **1997**, *75*, 1011–1022; b) M. Feigel, *J. Mol. Struct.* (*Theochem*) **1996**, *366*, 83–88; c) W. Weissensteiner, *Monatsh. Chem.* **1992**, *123*, 1135–1147; d) W. Weissensteiner, J. Scharf, K. Schlögl, *J. Org. Chem.* **1987**, *52*, 1210–1215; e) J. C. Barnes, J. D. Paton, J. R. Damewood, K. Mislow, *J. Org. Chem.* **1981**, *46*, 4975–4979; f) G. Montaudo, S. Caccamese, P. Finocchiaro, *J. Am. Chem. Soc.* **1971**, *93*, 4202–4207; g) D. Gust, K. Mislow, *J. Am. Chem. Soc.* **1973**, *95*, 1535–1547.

[13] Gaussian 98, Revision A.6, Gaussian, Inc., Pittsburgh PA, **1998**.

[14] A. García Martínez, J. Osío Barcina, A. Albert, F. H. Cano, L. R. Subramanian, *Tetrahedron Lett.* **1993**, *34*, 6753–6756.

[15] A. García Martínez, J. Osío Barcina, A. de Fresno Cerezo, R. Gutiérrez Rivas, *J. Am. Chem. Soc.* **1998**, *120*, 673–679.

[16] A. García Martínez, J. Osío Barcina, A. de Fresno Cerezo, A.-D. Schlüter, J. Frahn, Adv. Mater. 1999, 11, 27–31.

[17] A. García Martínez, J. Osío Barcina, A. de Fresno Cerezo, G. Rojo, F. Agulló-López, *J. Phys. Chem. B* **2000**, *104*, 43–47.

[18] A 1:1 stoichiometry has been reported (see ref. [5] by using Job's method of continuous variation. We have confirmed these results by means of the mole ratio method: K. A. Connors, *Binding Constants, The Measurement of Molecular Complex Stability*, Wiley, New York, **1987**, p. 26.

[19] a) H. A. Benesi, J. H. Hildebrand, *J. Am. Chem. Soc.* **1949**, *71*, 2703–2704; b) J.-L. Pierre, P. Baret, P. Chantemps, M. Armand, *J. Am. Chem. Soc.* **1981**, *103*, 2986–2988; c) M. Lämsä, J. Huuskonen, K. Rissanen, J. Pursiainen, *Chem. Eur. J.* **1998**, *4*, 84–92.

[20] E. L. Eliel, S. H. Wilen, L. N. Mander, *Stereochemistry of Organic Compounds*, Wiley, New York, **1994**, p. 601.

[21] The propeller conformation of the aryl groups of DPC in complex **A** has recently been reinvestigated and confirmed with the anisotropy of aromatic and carbonylic π bonds taken into account: C. A. Hunter, M. J. Packer, *Chem. Eur. J.* **1999**, *5*, 1891–1897; see also ref. [11d)].

[22] For a discussion about the factors affecting the energy of amide hydrogen bonds, see: L. Yu, H.-J. Schneider, *Eur. J. Org. Chem.* **1999**, 1619–1625.

[23] M. S. Searle, D. H. Williams, *J. Am. Chem. Soc.* 1992, 114, 10690–10697.

[24] P. G. Gassman, P. G. Pape *J. Org. Chem.* **1964**, *29*, 160–163.

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