
**Supramolecular Chemistry**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

# Molecular Recognition of Carbonyl Compounds by Uranyl-salophen Based Neutral Receptors Driven by Van Der Waals Forces

Valeria van Axel Castelli[a]; Antonella Dalla Cort[a]; Luigi Mandolini[a]; Valentina Pinto[a]; David N. Reinhoudt[b]; Fabrizio Ribaudo[a]; Cecilia Sanna[a]; Luca Schiaffino[a]; Bianca H. M. Snellink-Ruël[b]
[a] Dipartimento di Chimica and Centro CNR Meccanismi di Reazione, Università La Sapienza, Roma, Italy [b] Faculty of Chemical Technology, Supramolecular Chemistry and Technology (SMCT), University of Twente, Enschede, The Netherlands

Online publication date: 29 October 2010

**To cite this Article** Castelli, Valeria van Axel , Cort, Antonella Dalla , Mandolini, Luigi , Pinto, Valentina , Reinhoudt, David N. , Ribaudo, Fabrizio , Sanna, Cecilia , Schiaffino, Luca and Snellink-Ruël, Bianca H. M.(2002) 'Molecular Recognition of Carbonyl Compounds by Uranyl-salophen Based Neutral Receptors Driven by Van Der Waals Forces', Supramolecular Chemistry, 14: 2, 211 — 219
**To link to this Article: DOI:** 10.1080/10610270290026112
**URL:** http://dx.doi.org/10.1080/10610270290026112

*Supramolecular Chemistry*, 2002 Vol. 14 (2-3), pp. 211–219



# Molecular Recognition of Carbonyl Compounds by Uranyl-salophen Based Neutral Receptors Driven by Van Der Waals Forces

VALERIA VAN AXEL CASTELLI[a], ANTONELLA DALLA CORT[a], LUIGI MANDOLINI[a,*], VALENTINA PINTO[a], DAVID N. REINHOUDT[b], FABRIZIO RIBAUDO[a], CECILIA SANNA[a], LUCA SCHIAFFINO[a] and BIANCA H.M. SNELLINK-RUËL[b]

[a]*Dipartimento di Chimica and Centro CNR Meccanismi di Reazione, Università La Sapienza, Box 34, Roma 62, 00185 Roma, Italy;* [b]*University of Twente, Faculty of Chemical Technology, Supramolecular Chemistry and Technology (SMCT), P.O. Box 217, NL-7500 AE Enschede, The Netherlands*

**The complexation of the salophen-uranyl metallocleft 2 and of its half-cleft analogue 3 with enones and other carbonyl compounds was assessed in chloroform by UV–Vis titration and, occasionally, by FT-IR measurements. Complexes with receptors 2 and 3 are in all cases more stable than those with the control unsubstituted uranyl-salophen 1, showing that in addition to the primary binding force provided by coordination of the carbonyl oxygen to the uranium, a significant driving force for complexation, typically in the range of 2–3 kcal/mol, results from van der Waals interactions of the guest with the aromatic walls. Replacement of the phenyl group in 3 with larger aromatic residues to give 4 and 5, led to enhanced complex stabilities, due to more extended contact surfaces between host and guest.**

*Keywords*: Uranyl-salophen; van der Waals forces; Neutral molecule recognition; Enone guests; Ketone guests



## INTRODUCTION

The uranyl cation $UO_2^{2+}$ forms a robust complex (**1**) with the salophen ligand. Due to the well-known preference of the uranyl cation for pentagonal bipyramidal coordination [1,2], a fifth equatorial site is still available for coordination of an additional donor. Incorporation of the neutral unit **1** into more elaborate structures provided metallomacrocycles and metalloclefts for use in complexation of anions [3] and neutral molecules [4]. The hard Lewis acid character of the uranyl-salophen unit was further exploited in catalytic studies of nucleophilic addition to the carbonyl group of esters (acyl transfer reactions) [5] and to the activated double bond of enones (Michael-type additions) [6,7].

The present work deals with the use of uranyl-salophen based receptors in the molecular recognition of ketones and enones. Previous data obtained in the course of our catalytic studies [6,7] had shown that the complex **1** was an inherently weak binder of some ketones and enones, but with metallocleft **2**, where the distance between the nearly parallel phenyl groups is about 7 Å, very significant binding enhancements were obtained [8]. $^1$H NMR and FT-IR spectroscopic evidences showed [6,7] that in the host–guest complexes, the guest is bound via its carbonyl oxygen to the fifth coordination site of the uranium, and is located in the inside of the cleft (Fig. 1). Clearly, the cleft walls are responsible for the increased binding ability of **2** as compared to **1**.

In order to understand the nature of the stabilising interactions between the cleft walls and the guest, and to explore the scope of such interactions in the molecular recognition of ketones and enones, we have investigated and compared the binding abilities of uranyl-salophen compounds **1**, **2**, **3**, **4**, and **5** towards a large number of ketone and enone guests.

## EQUILIBRIUM MEASUREMENTS

Equilibrium measurements were carried out by means of a standard UV–Vis titration technique. Addition of increasing amounts of ketone guest to a

*Corresponding author.

ISSN 1061-0278 print/ISSN 1029-0478 online © 2002 Taylor & Francis Ltd
DOI: 10.1080/10610270290026112

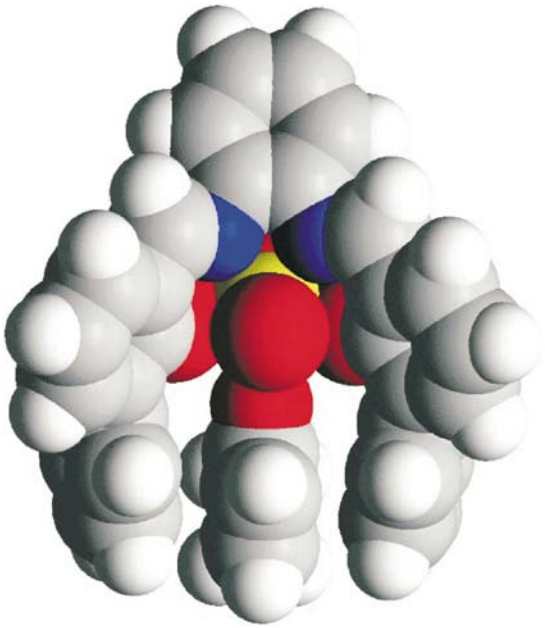
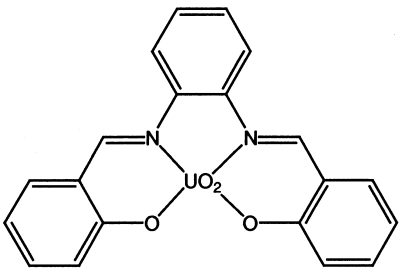
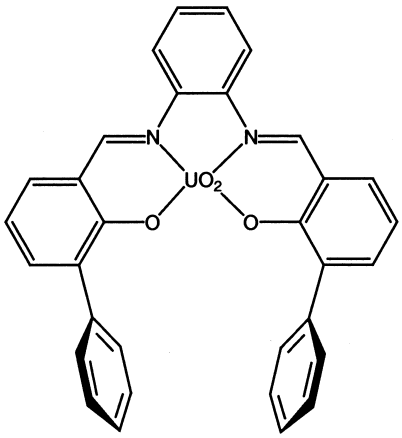


FIGURE 1 Computer drawn CPK model of the host-guest complex between metallocleft **2** and 2-cyclopenten-1-one.



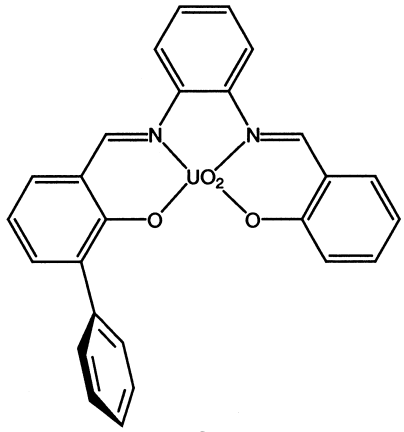


**1**



**2**

0.10–0.06 mM solution of a given uranyl-salophen complex in chloroform caused small, but reproducible absorbance changes in the neighbourhood of 430–440 nm (Fig. 2), where absorption of the ketone/enone guest is negligibly small, with the sole exception of perinaphthenone (see below). In a



**3**

number of cases involving complex **1**, titration experiments provided evidence for the existence of the association equilibrium but the small absorbance variations observed, accompanied by no significant curvature in the corresponding titration plots, did not allow an estimate of the low association constant ($K < 3\,M^{-1}$). In the other cases, titration plots were obtained that were consistent with a standard binding isotherm for 1:1 complexation (Fig. 2). Numerical values of the equilibrium constants were obtained by means of a non-linear curve fitting procedure.

Independent measurements based on FT-IR spectroscopy were carried out in selected cases. Addition of increasing amounts of **2** to a solution of 1-acetyl-1-cyclohexene in chloroform at 25°C caused a gradual decrease of the intensity of the carbonyl band at 1660 $cm^{-1}$ and the appearance of an increasingly

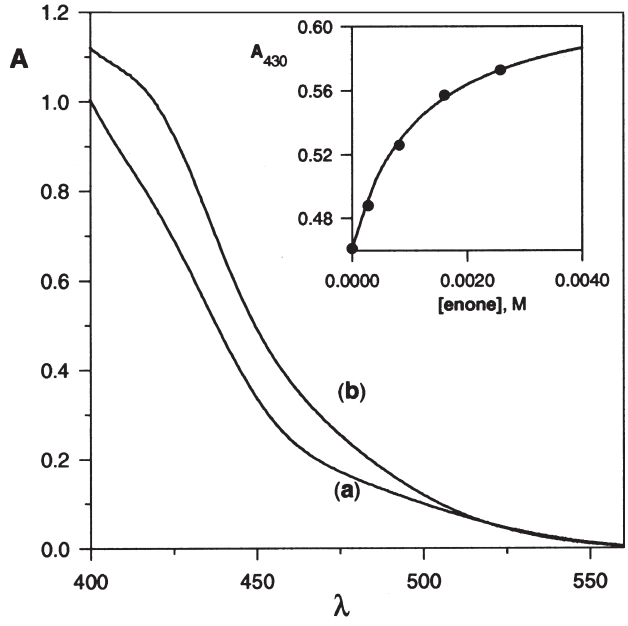



FIGURE 2 UV–Vis spectrum in $CHCl_3$ of: (a) 1 mM **3**; (b) 1 mM **3** + excess of 2-cyclopenten-1-one. A typical titration plot at $\lambda = 430$ nm is shown in the inset.

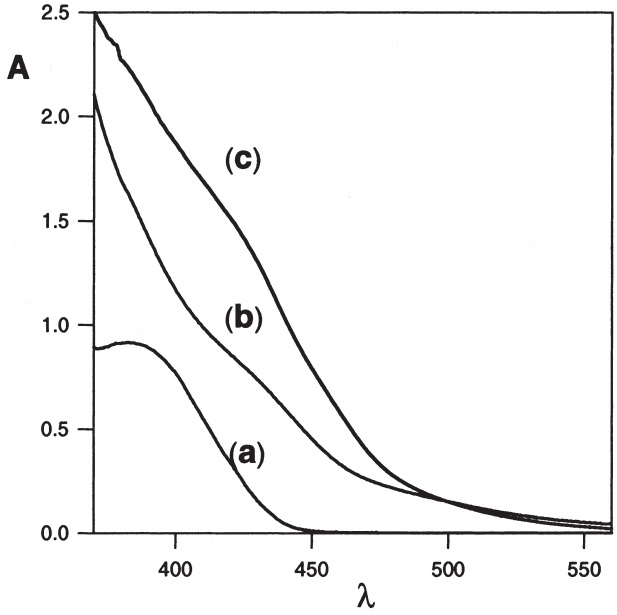



FIGURE 3 UV–Vis spectra in $CHCl_3$ of: (a) perinaphthenone; (b) receptor **5**; (c) equimolar mixture of the two reactants. The concentration of all species is $7.5 \times 10^{-5}$.

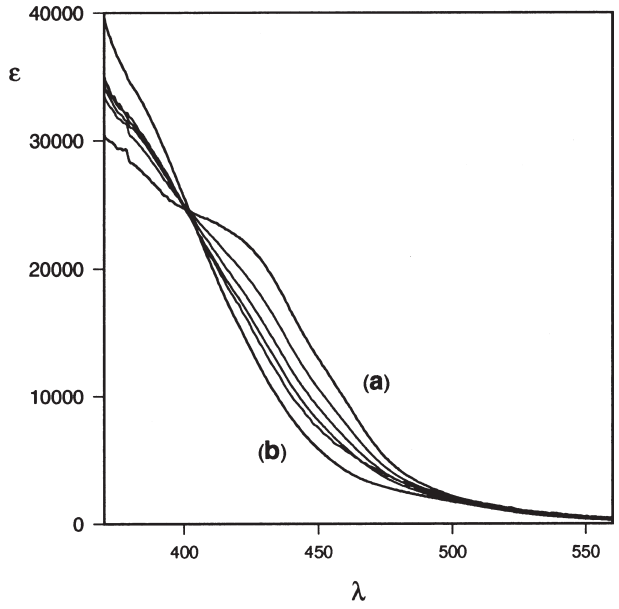



FIGURE 4 UV–Vis spectra in $CHCl_3$ of: (a) $\epsilon$ value of the 1:1 complex of **5** with perinaphthenone; (b) sum of the $\epsilon$ values of **5** and perinaphthenone. The intermediate curves from (a) to (b) are the apparent $\epsilon$ values of equimolar mixtures of perinaphthenone and **5**. Concentrations are $7.5 \times 10^{-4}$, $1.5 \times 10^{-4}$, $5.0 \times 10^{-5}$, $9.6 \times 10^{-6}$ M in the given order.



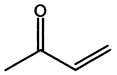
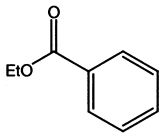
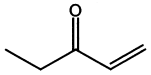
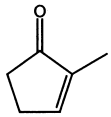
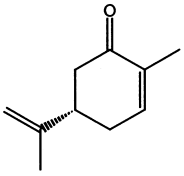
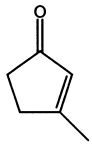
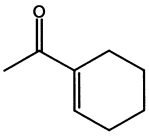
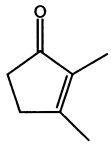
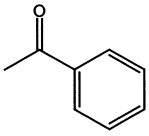
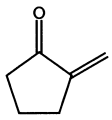
stronger band at 1620 $cm^{-1}$, which was attributed to the carbonyl coordinated to the uranyl. From the decrease in intensity of the band at 1660 $cm^{-1}$, a binding constant $K = 65 \pm 10\,M^{-1}$ was evaluated, which compares well to the value of $60 \pm 4\,M^{-1}$ from UV–Vis titration. Similar results were obtained for the complex of **2** with cyclopentanone.

Because the absorption of perinaphthenone is still significant in the 430–440 nm region, titration experiments were carried out at 470 nm, where perinaphthenone absorption is negligible (Fig. 3). Titration plots were consistent with a standard binding isotherm for 1:1 complexation, but absorbance variations were much larger than those observed in titrations not involving perinaphthenone. To rule out the occurrence of undesired side-reactions, possibly photoinduced during titration, an additional series of experiments was carried out. The results are summarized in Fig. 4. Curve (a) is the molar extinction coefficient ($\epsilon$) of the complex, and curve (b) is the sum of the $\epsilon$ values of the two reactants. The intermediate curves are the apparent $\epsilon$ values of varying concentrations of equimolar mixtures of perinaphthenone and **5** at which complexation is significant, but not complete. Thus, Fig. 4 gives spectral variations in a dilution experiment, in which the 1:1 complex is diluted until dissociation into its separate components is complete. The presence of a clean-cut isosbestic point confirms that interaction between perinaphthenone and **5** strictly adheres to 1:1 stoichiometry.

Although a detailed analysis of the UV–Vis spectral changes upon complexation is outside the scope of the present work, we note that complexation of perinaphthenone with a number of Lewis acids is known to cause significant bathochromic shifts [9]. Thus, we believe that a major contribution to the large absorbance variations observed in the titrations at 470 nm are simply due to the uranium-complexed perinaphthenone, and not to a charge-transfer band resulting from a charge-transfer interaction with the pyrenyl moiety in **5**. That this conclusion is correct is confirmed by the finding that a similar bathochromic shift was experienced by perinaphthenone upon complexation with **1**, where the possibility of a charge-transfer interaction is clearly out of the question.

The results of equilibrium measurements are summarized in Tables I–III. The data collected in Table I, when combined with the analogous data listed in the first and second column of Table II, which are available from previous investigations, allow an assessment of the influence of the cleft walls on the binding ability of metallocleft **2**. The effect of reducing the $\pi$ surfaces from two to one is illustrated in Table II, where the receptor properties of metallocleft **2** are compared with those of the related half-cleft **3**. Finally, the effect of an increase in the $\pi$ surface available for interaction with the guest is shown in Table III, where equilibrium constants for association of a number of enones with half-clefts **3**, **4**, and **5** are compared.

TABLE I Association constants ($K$, $M^{-1}$) for complexes between receptors **1** and **2** with α,β-unsaturated carbonyl compounds in $CHCl_3$ at 25°C

| | **1** | **2** | | **1** | **2** |
|---|---|---|---|---|---|
|  | <3 | 46 ± 6 |  | <3 | 22 ± 1 |
|  | <3 | 160 ± 20 |  | 16 ± 2 | 170 ± 5 |
|  | 3.6 ± 0.6 | 92 ± 4 |  | 33 ± 6 | 610 ± 15 |
|  | 5.0 ± 0.3 | 60 ± 4* |  | 46 ± 2 | 470 ± 20 |
|  | <3 | 23 ± 2 |  | 3.0 ± 0.2 | 46 ± 2 |

From UV–Vis titrations. Error limits are calculated as $\pm 2\sigma$ confidence limit. * $K = 65 \pm 10\,M^{-1}$ from FT-IR measurements.



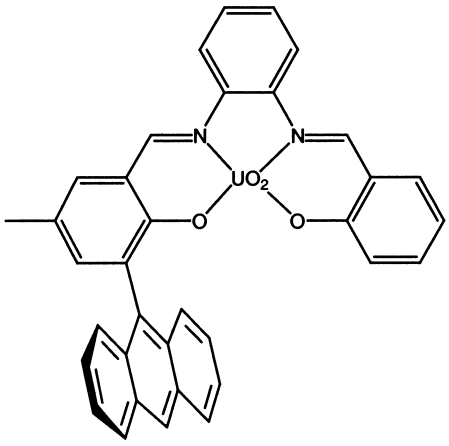
## RESULTS AND DISCUSSION

The parent uranyl-salophen complex **1**, in which the sole driving force for association is provided by the Lewis acid–base interaction between the uranyl and the carbonyl oxygen, forms weak complexes with the carbonyl compounds investigated. The equilibrium constants are too low to measure with any precision for a number of substrates, namely, acetophenone and ethyl benzoate, the saturated ketones, methyl vinyl ketone and ethyl vinyl ketone. For the remaining substrates equilibrium constants fall in the measurable range, the largest values being found with the 3-methyl and 2,3-dimethyl derivatives of 2-cyclopenten-1-one.

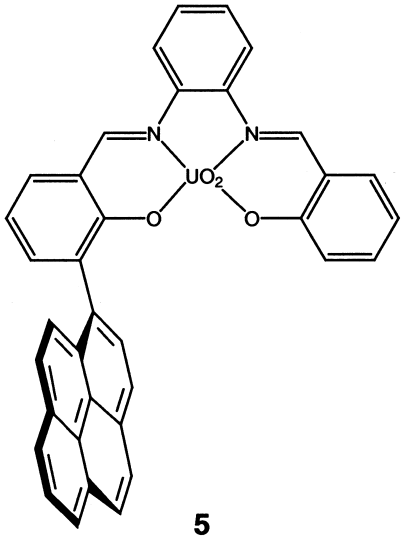
The undeniable tendency of the α, β-unsaturated ketones to form stronger complexes than their saturated counterparts provides a clear indication that the Lewis basicity of the carbonyl is significantly enhanced by conjugation with the double bond. The large influence on complex formation of the methyl group in the β-position of 2-cyclopenten-1-one is likely to be ascribed to hyperconjugative interaction of the methyl substituent with the carbonyl group, as shown in **6**. Similarly, the finding that among the *gem*-dimethyl derivatives of 2-cyclohexen-1-one the strongest complex is formed by the 4,4-isomer strongly suggests that hyperconjugation involving C–C bonds [10,11] (**7**) is important. The absence of alkyl substituents on the double bond accounts well for the very weak associations of the vinyl ketones. The low binding affinity of cyclopentanone-2-methylene toward **1** is due to the lack of a β-alkyl substituent and, presumably, to steric repulsion of the exocyclic methylene with the salophen moiety and/or with the uranyl oxygens [12]†.

Complexes with metallocleft **2** are in all cases more stable than with the parent compound **1**.

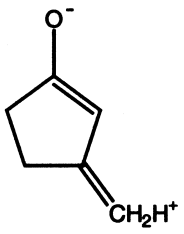
†The complex of SnCl4 and (E)-2-heptenal and the BF3 complexes of (E)-2-heptenal and 2-methylacroleyn are primarily in the s-*trans* conformation in solution. This indicates that the s-*cis* conformation of the given α,β-unsaturated carbonyl compounds are inherently less prone to complexation than the s-*trans* conformations. It is difficult to say whether and to what an extent the low association tendency of cyclopentanone-2-methylene, in which the s-*cis* conformation is geometrically enforced, is related to the above findings.



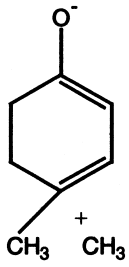

**4**




**5**




**6**




**7**

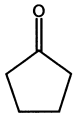
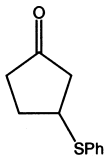
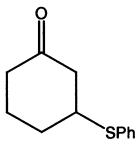
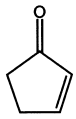
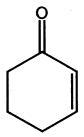
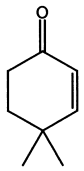
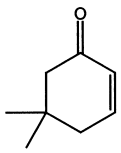
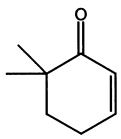
Enhancements of complex stability brought about by the cleft walls range from 10- to 100-fold, with the sole exception of 6,6-dimethyl-2-cyclohexen-1-one, for which a much lower effect is observed. It is remarkable that the above stability enhancements are observed in chloroform, where solvophobic interactions are likely to play a very minor role, if any, and where there are strong interactions, presumably hydrogen bonding in nature [13], with the ketone guest. The obvious conclusion which emerges from the data is that attractive interactions of the van der Waals type, conventionally labelled as CH–π [14] and π–π [15,16] interactions, are established between the aromatic cleft walls and the guest. These attractive forces add to the primary binding force provided by coordination of the carbonyl oxygen to the metal centre. Remarkably, $\Delta\Delta G^\circ$ contributions arising from the above weak forces amount to 2 to 3 kcal/mol in the most favourable cases. This is somewhat surprising, but not unreasonable, if one considers that the host can adjust itself for optimal interaction with the guest by means of very modest rotations around the C–C bonds connecting the phenyl groups to the salophen moiety. Hence little or no conformational reorganization in the host is required upon complexation and, consequently, a relative large binding free energy can result if several pairwise weak interactions are established between the guest and the highly preorganized host.

The source of the above forces can be broken down to dipole–dipole, induction, and London dispersion forces. It is not easy to make exact distinctions between different mechanisms, but there are indications of the dominance of dispersion forces in CH–π interactions [17]. That the role played in our systems by π–π interactions is comparable or even lower than that played by CH–π interactions is suggested by the observation that the enhancement of complex stability on going from **1** to **2** is larger for cyclopentanone ($> 140/3 = 47$) than for 2-cyclopenten-1-one ($460/14 = 33$).

The tight fit between molecular surfaces required by full contact of several atoms in the guest with a corresponding number of atoms in the host renders complexation with **2** more sterically demanding than with **1**. This is shown, for example, by the finding that the affinities of 2-cyclopenten-1-one and its 2-methyl derivative toward **1** are very nearly the same, but the former is complexed more strongly by **2**. An illustration of the adverse effect of substituents close to the carbonyl is given by 6,6-dimethyl-2-cyclohexen-1-one, whose affinity towards **2** is the lowest in the lot of investigated substrates.

Inspection of the third column in Table II shows that the receptor properties of **3**, where only one phenyl group is available for binding to the guest, are comparable to, or even larger than those of

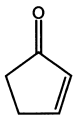
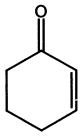
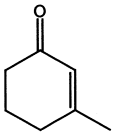
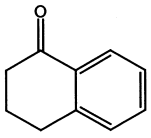
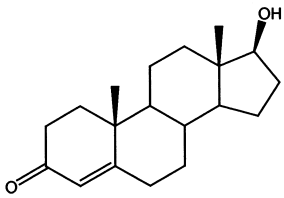
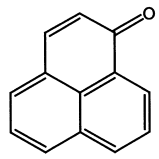
TABLE II Association constants ($K$, $M^{-1}$) for complexes between receptors **1**, **2**, and **3** with α, β-unsaturated carbonyl compounds in $CHCl_3$ at 25°C

| | **1*** | **2*** | **3** |
|---|---|---|---|
|  | <3 | 140 ± 20† | 258 ± 28 |
|  | <3 | 68 ± 6 | 135 ± 16 |
|  | <3 | 100 ± 10 | 86 ± 14 |
|  | 14 ± 1 | 460 ± 40‡ | 870 ± 120 |
|  | 7.6 ± 0.6 | 900 ± 200¶ | 320 ± 50 |
|  | 17 ± 2 | 820 ± 150§ | 530 ± 80 |
|  | 3.7 ± 1.2 | 130 ± 16 | 330 ± 40 |
|  | 3.2 ± 0.4 | 6.4 ± 1.4 | 90 ± 8 |

From UV–Vis titrations unless otherwise stated. Error limits are calculated as $\pm 2\sigma$. *From Refs. [6,7]. †$K = 136 \pm 20\,M^{-1}$ from FT-IR measurements. ‡$K = 520 \pm 80\,M^{-1}$ from $^1H$ NMR titration. ¶ From $^1H$ NMR titration. §$K = 760 \pm 100\,M^{-1}$ from $^1H$ NMR titration.

metallocleft **2** in a number of cases. This finding strongly indicates that the strict complementarity requirement for optimal multisite van der Waals interactions between the guest and cleft walls is hardly fulfilled simultaneously by either wall of receptor **2**. In fact, it is even conceivable that some of the internuclear distances in complexes with **2** are forced by the rigid geometry of the cleft to lie in the repulsive region. This hypothesis might provide an explanation for the lower affinity of **2** compared with **3** towards a number of guests. Again an extreme situation is offered by 6,6-dimethyl-2-cyclohexen-1-one, whose affinity

TABLE III Association constants ($K$, $M^{-1}$) for the complexes of receptors **3**, **4**, and **5** with α, β-unsaturated carbonyl compounds in $CHCl_3$ at 25°C

| | 3 | 4 | 5 |
|---|---|---|---|
|  | 870 ± 100 | 1800 ± 40 | 1700 ± 200 |
|  | 330 ± 50 | 610 ± 40 | 530 ± 530 |
|  | 1200 ± 100 | –* | 1600 ± 100 |
|  | 250 ± 20 | 360 ± 30 | 530 ± 30 |
|  | 1390 ± 100 | –* | 2940 ± 100 |
|  | 1170 ± 80† | 2010 ± 110† | 8000 ± 400† |

From UV–Vis titrations. Error limits are calculated as $\pm 2\sigma$. * Not determined. † The association constant of perinaphthenone with **1** under the same conditions is $14 \pm 2\,M^{-1}$.

towards **3** is some 30-fold higher than that towards **2**, showing that the bulky *gem*-dimethyl group in position 6 strongly hinders complexation with **2**, but only to a limited extent with **3**.

The association constants of receptors **3**, **4**, and **5** with a number of enone guests in chloroform at 25°C are listed in Table III. The phenyl side wall of half-cleft **3** was replaced by 9-anthracenyl and 1-pyrenyl groups in an effort to increase the van der Waals contacts between the host and the guest. There is indeed a general tendency for the association constants to be larger with receptors **4** and **5** than with **3**, but the stability increase amounts to a factor of 2 in most cases, or even less. The sole exception is the perinaphthenone–**5** pair, for which an equilibrium constant of $8000\,M^{-1}$ was measured, which is 4- and 7-fold larger than the corresponding quantities found with receptors **4** and **3**, respectively. The large affinity between **5** and perinaphthenone most likely arises from a wide contact surface between the guest and pyrene moiety, as illustrated in Fig. 5. Compared with the control unsubstituted uranyl-salophen **1** (see footnote † to Table III), the pyrene receptor **5** shows a 570-fold increase in binding constant, which corresponds to a stacking interaction of 3.8 kcal/mol, presumably arising from a combination of dispersion and π–π interactions.

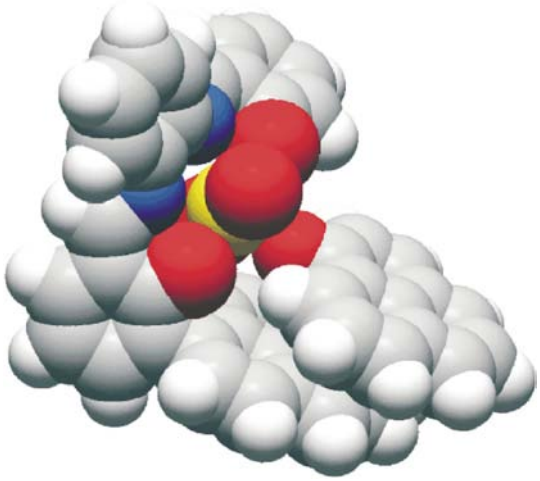


FIGURE 5 Computer drawn CPK model of the host–guest complex between receptor **5** and perinaphthenone.

## CONCLUSIONS

Complexation data reported in this work add to our knowledge of molecular recognition of neutral molecules in the absence of solvophobic effects. The data show that even very weak van der Waals interactions can be exploited for efficient recognition of carbonyl compounds, if coordination of the carbonyl group to the uranyl provides for the primary binding force between host and guest, and very little conformational reorganization in the host is required upon complexation.

Partial rotations around the C–C bonds connecting the phenyl groups to the salophen moiety in an otherwise rigid receptor do not permit the geometry of **2** to be adjusted in such a way as to allow optimal interactions of both phenyl groups with the guest. Consequently, the receptor properties of metallocleft **2** do not differ very much from those of its half-cleft analogue **3** in general. Noteworthy is the behaviour of 6,6-dimethyl-2-cyclohexen-1-one which is hosted much better by the more open structure of **3** because of the bulky *gem*-dimethyl group close to the carbonyl.

An increase in the surface of the aromatic wall of **3** causes complex stability enhancements due to the resulting increase in the contact surface between host and guest. Remarkably, an affinity as high as $K = 8000\,M^{-1}$ is observed for the perinaphthenone–**5** pair.

In previous work [6,7], we have reported that metallocleft **2** activates a bound enone towards Michael type thiol addition, leading to a catalytic process characterized by high turnover efficiency and high substrate selectivity. The catalytic properties of half-clefts **3**–**5** are now under current investigation. The results of such an investigation will be reported in due course.

## EXPERIMENTAL SECTION

### Instruments and Methods

UV–Vis spectra were carried out on a Perkin Elmer Lambda 18 spectrophotometer, equipped with a thermostated cell holder. The IR spectra were obtained on a Perkin–Elmer 1720-XFT spectrophotometer. Nonlinear least-squares calculations were carried out using the programme SigmaPlot for Windows, 1.02 (Jandel Scientific).

### Materials

Salophen-uranyl complexes **1** and **2** were available from a previous work [6]. The syntheses of complexes **3**–**5** will be reported in a subsequent work. Cyclopentanone-2-methylene was prepared and purified according to a literature method [18]. All other guests were commercially available. 2-Cyclopenten-1-one and 2-cyclohexen-1-one were purified by distillation under reduced pressure to remove impurities which interfered with the UV–Vis measurements. The vinylketones were distilled under reduced pressure from calcium hydride immediately before use. This was a necessary prerequisite for obtaining reproducible titration plots.

### *Acknowledgements*

Work carried out in the frame of COST D11, Supramolecular Chemistry. Thanks for financial support are due to MURST, Progetto Dispositivi Supramolecolari.

### *References*

[1] Bandoli, G., Clemente, D.A., Croatto, U., Vidali, M. and Vigato, P.A. (1971), *J. Chem. Soc. Chem. Commun.*, 1330.
[2] Van Staveren, C.J., Fenton, D.E., Reinhoudt, D.N., van Eerden, J. and Harkema, S. (1987), *J. Am. Chem. Soc.* **109**, 3456.
[3] Rudkevich, D.M., Huck, W.T.S., van Veggel, F.C.J.M. and Reinhoudt, D.N. (1994) "Metallomacrocycles and -clefts: receptors for neutral molecules and anions", In: Fabbrizzi, L. and Poggi, A., eds, *Transition Metals in Supramolecular Chemistry NATO ASI Series* (No. 448), Series C: Mathematical and Physical Science, (Kluwer, Dordrecht), pp 329–349.
[4] Van Doorn, A.R., Verboom, W. and Reinhoudt, D.N. (1993) "Molecular recognition of neutral molecules by synthetic receptors", In: Gokel, G.W., eds, *Advances in Supramolecular Chemistry* (JAI Press, Greenwich) **Vol. 3**, pp 159–206.
[5] van Axel Castelli, V., Cacciapaglia, R., Chiosis, G., van Veggel, F.C.J.M., Mandolini, L. and Reinhoudt, D.N. (1996), *Inorg. Chim. Acta* **246**, 181.
[6] van Axel Castelli, V., Dalla Cort, A., Mandolini, L. and Reinhoudt, D.N. (1998), *J. Am. Chem. Soc.* **120**, 12688.
[7] van Axel Castelli, V., Dalla Cort, A., Mandolini, L., Reinhoudt, D.N. and Schiaffino, L. (2000), *Chem. Eur. J.* **6**, 1193.
[8] van Doorn, A.R., Bos, M., Harkema, S., van Eerden, J., Verboom, W. and Reinhoudt, D.N. (1991), *J. Org. Chem.* **56**, 2371.
[9] Mohammad, A., Satchell, D.P.N. and Satchell, R.S. (1967), *J. Chem. Soc. (B)*, 723.

[10] Bingham, R.C. and Schleyer, P.V.R. (1971), *J. Am. Chem. Soc.* **93**, 3189.
[11] Ebeil, K. and Mayring, L. (1976), *Angew. Chem. Int. Ed. Engl.* **15**, 554.
[12] Corey, E.J., Loh, T.-P., Sarshar, S. and Azimioara, M. (1992), *Tetrahedron Lett.* **62**, 6945.
[13] Hammett, L.P. (1970) *Physical Organic Chemistry* (McGraw-Hill, New York), p 249.
[14] Nishio, M., Hirota, M. and Umezawa, Y. (1998) *The CH/π Interaction. Evidence, Nature, and Consequences* (Wiley-VCH, New York).
[15] Hunter, C.A., Lawson, K.R., Perkins, J. and Urch, C.J. (2001), *J. Chem. Soc., Perkin Trans.* **2**, 651.
[16] Hunter, C.A. and Sanders, J.K.M. (1990), *J. Am. Chem. Soc.* **112**, 5525.
[17] Kim, E., Paliwal, S. and Wilcox, C.S. (1998), *J. Am. Chem. Soc.* **120**, 11192.
[18] Mannich, C. and Schaller, P. (1938), *Arch. Pharmaz. Ber. Dtsch. Pharmaz.* **276**, 575.