

Solid-state Structures of *N*-Substituted Michler's Ketones and Their Relation to Solvatochromism

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The solvatochromism ($v_{\max}$) of *N*-substituted Michler's ketones – including 4'-[bis(2-acetoxyethyl)amino]-4-(dimethylamino)benzophenone [MK(OAc)₂, **1a**], 4,4'-bis(diethylamino)benzophenone [MK(NEt₂)₂, **1e**], 4,4'-bis(4-ethoxycarbonylpiperazino)benzophenone [MK(pipOEt)₂, **2a**], 4,4'-bis(piperidino)benzophenone [MK(pip)₂, **2b**], 4,4'-bis(morpholino)benzophenone [MK(mor)₂, **2c**], 4,4'-bis(piperazino)benzophenone [MK(pipaz)₂, **2d**], 4,4'-bis[4-(2-hydroxyethyl)piperazino]benzophenone [MK(pipazOH)₂, **2e**] and 1,4-bis(4-benzoylphenyl)piperazine (BBP, **3**) – has been studied at 298 K in various solvents with wide ranging dipolarities and hydrogen-bonding abilities. The solvatochromic properties ($v_{\max}$)_s = ($v_{\max}$)₀ + $s\pi^* + aa + b\beta$ have been analysed in terms of the Kamlet–Taft linear solvation energy (LSE) relationship. The effect of the solvent on the UV/Vis spectral characteristics ($v_{\max}$) has been determined quantitatively for all compounds in terms of the Kamlet–Taft solvent-independent correlation coefficients s , a , and b . It was found to be mainly the dipolarity/polarizability (π^*) and hydrogen bond acidity (a) of the solvent that contribute to the bathochromic UV/Vis band shift. As strongly basic sites are present as substituents

at the peripheries of the molecules, protonation takes place at the secondary nitrogen atom of, for example, MK(pipaz)₂ (**2d**) in strongly hydrogen bond-donating (HBD) solvents. This specific type of substitution therefore gives rise to an ambiguous solvatochromic property, which makes the basicity (β term) of the solvent important. The solid-state structures of **2b** (C₂₃H₂₈N₂O), **2c** (C₂₁H₂₄N₂O₃), and **3** (C₃₀H₂₆N₂O₂) have been determined by single-crystal X-ray structure analysis. Compound **2b** crystallizes in the trigonal space group $P3_121$ with $a = 948.11(11)$, $b = 948.11(11)$, $c = 1818.0(3)$ pm, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$ and $Z = 3$, whereas **2c** crystallizes in the orthorhombic space group $Pna2_1$ with $a = 1259.9(2)$, $b = 910.16(17)$, $c = 1586.2(3)$ pm, $\alpha = \beta = \gamma = 90^\circ$ and $Z = 4$. Compound **3** crystallizes in the triclinic space group $P1$ with $a = 1034.0(2)$, $b = 1079.9(2)$, $c = 1127.2(2)$ pm, $\alpha = 72.062(4)$, $\beta = 73.361(4)$, $\gamma = 74.549(4)^\circ$ and $Z = 2$. The UV/Vis band shifts are comparatively discussed with regard to the LSE relationships and the results of the solid-state structure determinations.

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Introduction

Examination of chromophoric aggregates and supramolecular structures by UV/Vis spectroscopy is an experimental challenge and of importance both for academic research and for practical applications in nano-science.^[1–6] For this objective, exact knowledge of the solid-state structure (e.g., by solid-state X-ray structure analysis) in relation to the corresponding UV/Vis spectrum is required. The UV/Vis spectral variation of molecular aggregates as a function of solid-state structure should play a significant role in en-

abling the effects of substituents on intermolecular interactions in the solid state to be determined. This requires the choice of suitable model compounds that show colour changes as a function of the nature of accumulation process. Recently, we have shown that a hydrophilically substituted solvatochromic compound of the Michler's ketone type (4'-[bis(2-hydroxyethyl)amino]-4-(dimethylamino)benzophenone, MK(OH)₂^[7]) has a significant new UV/Vis band that can be readily explained in terms of the intermolecular interaction between the polar HBD (hydrogen bond-donating) substituents in the periphery and the polar HBA (hydrogen bond-accepting) group in the chromophore.

Because various Michler's ketones are readily available through nucleophilic substitution of 4,4'-difluorobenzophenone with secondary amines,^[7,8] this class of compound was chosen for preliminary studies. Furthermore, compounds of this type have already been widely investigated thanks to their outstanding solvatochromic and photophysical properties.^[7–15] They are also of importance as precursors for the production of di- and triphenylmethylium ions.^[16–18]

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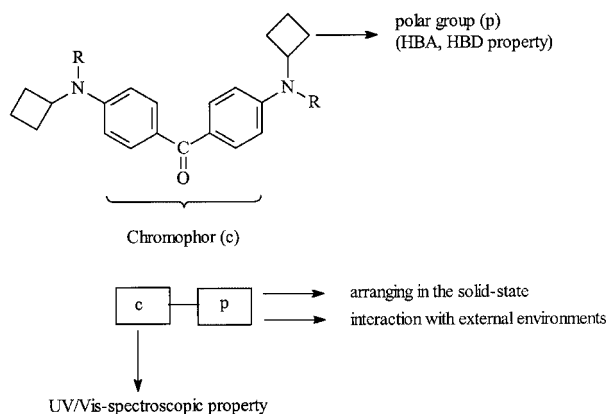
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The solvatochromic properties of Michler's ketone – 4,4'-bis(dimethylamino)benzophenone (**MK**) – and related compounds have become established as a suitable tool for investigation of the polarities of various liquids^[7,12–14] and of solid environments such as functionalized silica particles, α -amino acid crystals, polyamino acids, and synthetic and native macromolecular materials.^[19–26]

It is to be expected that substituents at the periphery of the chromophore should have an effect like that of external solvents. This concept is outlined in Scheme 1.



Scheme 1. Schematic illustration of the molecular design concepts of Michler's ketones

For this preliminary work, we chose the **MK** derivatives shown in Scheme 2.

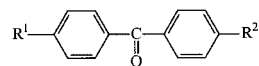
Solvatochromism has been used as a tool for elucidation of the respective influences of dipolarity/polarizability, acidity and basicity of the environment on the solvatochromic band shift of the respective compound class as function of its substituents. For this purpose we used the well established and accepted Kamlet–Taft linear solvation energy (LSE) relationship.^[27–37]

The simplified Kamlet–Taft equation applied to single solvatochromic shifts, $XYZ = 1/\lambda_{\max} = \nu_{\max}(\text{probe})$,^[30,34–37] is given in Equation (1).

$$XYZ = (XYZ)_0 + a\alpha + b\beta + s(\pi^* + d\delta) \quad (1)$$

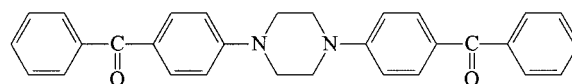
$(XYZ)_0$ is the solute property of a reference system (a nonpolar medium, for example), α describes the HBD (hydrogen bond-donating) acidity, β the HBA (hydrogen bond-accepting) ability, and π^* the dipolarity/polarizability of the respective solvent. δ is a polarizability correction term, which is 1.0 for aromatic, 0.5 for polyhalogenated and zero for aliphatic solvents, while a , b , s , and d are solvent-independent regression coefficients.^[30,35,36]

The linking of two identical solvatochromic chromophores through a rigid spacer (piperazine) was also used as a model in order to study the influence of the molecular polarity of the chromophore itself on its own counterpart. The two chromophores are oppositely arranged with regard to their individual dipolar directions (Scheme 3).



R ¹	R ²	Abbreviation	No
		MK(OAc) ₂	1a
		MK(OH) ₂	1b
		MK	1c
		MK(OH) ₄	1d
		MK(NEt ₂) ₂	1e
		MK(pipOEt) ₂	2a
		MK(pip) ₂	2b
		MK(mor) ₂	2c
		MK(pipaz) ₂	2d
		MK(pipazOH) ₂	2e

Scheme 2. Michler's ketones **1a–e** and **2a–e** used in this work



Scheme 3. 1,4-Bis(4-benzoylphenyl)piperazine (BBP, **3**)

The specific question to be answered is: do the two solvatochromic moieties compensate their dipolarity or not and how is this effect detectable by means of UV/Vis spectroscopy?

The objective of this work is to examine the solvatochromic properties of the novel Michler's ketones **1a**, **1e**, **2a–e**, and **3** (Schemes 2 and 3) in terms of the Kamlet–Taft solvent parameter set, and to study the effect of the crystal structure on the UV/Vis spectral behaviour of these compounds as a function of *N*-substituent. In the discussion, we also take into account results of further studies on MK^[12] (**1c**) and the two hydrophilic derivatives MK(OH)₂ (**1b**) and MK(OH)₄^[7] (**1d**) (Scheme 2).

Results and Discussion

Solvatochromic Measurements

The UV/Vis absorption spectra around the solvatochromic UV/Vis bands (the longest-wavelength band of the π -

Table 1. UV/Vis absorption maxima for MK(OAc)₂ (**1a**), MK(NEt₂)₂ (**1e**), MK(pipOEt)₂ (**2a**), MK(pip)₂ (**2b**), MK(mor)₂ (**2c**), MK(pipaz)₂ (**2d**), MK(pipazOH)₂ (**2e**), and BBP (**3**) in 32 solvents of different polarity and hydrogen bond ability

Solvent	$\nu_{\max}/10^3 \text{ cm}^{-1}$ (1a)	$\nu_{\max}/10^3 \text{ cm}^{-1}$ (1e)	$\nu_{\max}/10^3 \text{ cm}^{-1}$ (2a)	$\nu_{\max}/10^3 \text{ cm}^{-1}$ (2b)	$\nu_{\max}/10^3 \text{ cm}^{-1}$ (2c)	$\nu_{\max}/10^3 \text{ cm}^{-1}$ (2d)	$\nu_{\max}/10^3 \text{ cm}^{-1}$ (2e)	$\nu_{\max}/10^3 \text{ cm}^{-1}$ (3)
Cyclohexane	30.03	29.33	30.67	29.94	30.67	[a]	30.86	30.86
Triethylamine	29.94	29.15	30.58	29.85	30.58	29.94	30.21	30.30
Diethyl ether	29.67	28.99	30.30	29.41	30.30	29.76	29.94	30.30
Tetrachloromethane	29.41	28.74	30.12	29.15	30.03	29.33	30.40	30.21
<i>p</i> -Xylene	29.15	28.49	29.76	28.99	29.85	29.50	30.00	29.85
Toluene	29.07	28.49	29.67	28.90	29.76	29.33	29.94	29.67
Tetrahydrofuran	28.99	28.41	29.59	28.90	29.67	29.15	29.67	29.41
1,2-Dimethoxyethane	28.99	28.41	29.50	28.90	29.76	29.15	29.50	29.15
Ethyl acetate	28.90	28.52	29.24	28.99	29.85	29.33	29.76	29.67
1,4-Dioxane	28.90	28.41	29.50	28.82	29.33	29.15	29.85	29.59
Benzene	28.90	28.33	29.41	28.74	29.50	29.24	29.85	29.59
Acetone	28.82	28.01	29.33	28.33	28.82	28.65	29.50	29.15
Dichloromethane	28.49	27.62	29.15	28.17	29.24	28.90	29.33	28.99
1,2-Dichloroethane	28.49	27.78	29.15	28.25	28.90	28.90	29.33	29.07
Chloroform	28.41	27.40	29.15	28.09	28.99	28.82	29.33	28.99
Acetonitrile	28.41	27.72	28.99	28.25	29.15	28.82	29.41	28.90
<i>N,N</i> -Dimethylacetamide	28.33	27.62	28.82	28.17	28.74	28.41	29.07	28.65
1,1,2,2-Tetrachloroethane	28.25	27.25	28.74	27.62	28.90	29.50	28.90	28.65
<i>N,N</i> -Dimethylformamide	28.25	27.55	28.82	28.09	28.99	28.41	28.99	28.65
Pyridine	28.25	27.40	28.82	27.93	28.90	28.33	28.90	28.65
Benzonitrile	28.01	27.32	28.74	27.93	28.65	28.33	27.25	28.25
1-Octanol	27.93	26.88	28.90	27.78	28.90	28.49	29.07	28.99
Dimethyl sulfoxide	27.86	27.10	28.41	27.70	28.57	28.01	28.64	28.17
1-Butanol	27.70	26.74	28.65	27.55	28.82	28.33	28.82	28.65
Ethanol	27.62	26.74	28.65	27.62	28.82	28.65	28.74	28.41
Acetic acid	27.62	26.25	28.17	27.03	28.49	29.41	30.21	28.00
Methanol	27.40	26.46	28.57	27.32	28.74	28.41	28.82	28.17
Formamide	26.95	26.04	27.86	26.81	28.09	28.90	29.41	28.99
Ethane-1,2-diol	26.74	25.97	27.78	26.67	28.09	28.74	29.85	28.57
Water	26.39	[a]	[a]	[a]	[a]	28.49	29.33	[a]
2,2,2-Trifluoroethanol	26.04	24.88	27.25	25.97	27.62	28.33	28.49	27.17
1,1,1,3,3,3-Hexafluoro-2-propanol	25.19	24.96	26.04	25.06	26.60	29.24	29.94	26.11

[a] Probe is insoluble in this solvent.

π^* transition) of **1a**, **1e**, **2a–e**, and **3** were measured in 32 common solvents at 293 K as shown in Table 1. The solvents used were those with wide ranging properties and for which α , β and π^* were known.^[38]

Overall, as the solvent polarity increases from cyclohexane (CH) to 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) (Table 1), the UV/Vis absorption spectra of MK(OAc)₂ (**1a**), MK(NEt₂)₂ (**1e**), MK(pipOEt)₂ (**2a**), MK(pip)₂ (**2b**), MK(mor)₂ (**2c**), and BBP (**3**) show a significant bathochromic shift of the long-wavelength UV/Vis band. A representative series of UV/Vis spectra is shown in Figure 1 for compound **3**.

The bathochromicity of the solvatochromic UV/Vis absorption bands of Michler's ketones was as theoretically expected and consequently in agreement with established results.^[9–12] This result as a whole indicates that these compounds are more dipolar in their excited singlet states than in their ground states. For **2e** and **2d**, however, the magnitude of the positive solvatochromic shift is lower, and also shows unprecedented UV/Vis absorption band shifts as a function of solvent polarity. The solvatochromism of these two compounds is therefore discussed separately (see below).

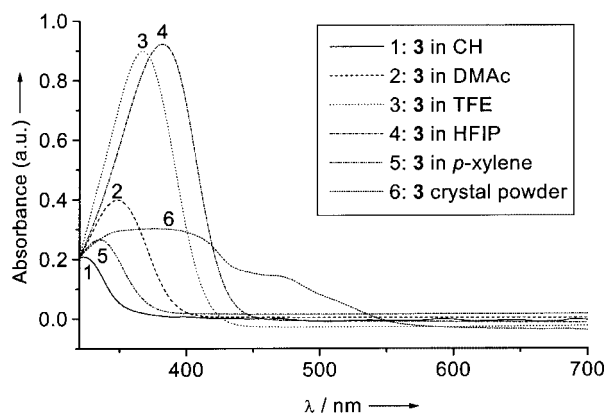


Figure 1. UV/Vis absorption spectra of BBP (**3**) in different solvents – cyclohexane (CH), *p*-xylene, dimethyl sulfoxide (DMSO), 2,2,2-trifluoroethanol (TFE), and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) – and reflection spectrum of the crystal powder

Results from multiple square analyses of the $\nu_{\max}$ values of the MK derivatives measured in the 32 solvents used, with the Kamlet–Taft solvent parameters, are summarized in Table 2.

Table 2. Values of the solvent-independent correlation coefficients (a , b , and s of the Kamlet–Taft parameters α , β , and π^*), solute property of a reference system (XYZ)₀, standard deviation (SD) and number of solvents (n) for the solvatochromism of MK(OAc)₂ (**1a**), MK(NEt₂)₂ (**1e**), MK(pipOEt)₂ (**2a**), MK(pip)₂ (**2b**), MK(mor)₂ (**2c**), MK(pipaz)₂ (**2d**), MK(pipazOH)₂ (**2e**), and BBP (**3**)

Compound	(XYZ) ₀	a	b	s	r	SD	Probe > F	n
MK(OAc) ₂	29.964	−1.502		−1.832	0.968	0.285	< 0.0001	32
	29.938	−1.502	0.080	−1.841	0.968	0.289	< 0.0001	32
	28.846	−1.670			0.873	0.546	< 0.0001	32
	30.096	−1.656	0.069	−2.055	0.985	0.195	< 0.0001	31 ^[a]
	30.118	−1.656		−2.047	0.985	0.192	< 0.0001	31 ^[a]
MK(NEt ₂) ₂	29.478	−1.774	−0.069	−2.142	0.985	0.207	< 0.0001	31 ^[b]
	29.456	−1.774		−2.149	0.985	0.204	< 0.0001	31 ^[b]
	28.129	−1.859			0.866	0.577	< 0.0001	31 ^[b]
	30.756	−1.355		−2.110	0.976	0.213	< 0.0001	31 ^[b]
	30.703	−1.355	0.162	−2.127	0.975	0.212	< 0.0001	31 ^[b]
MK(pipOEt) ₂	29.454	−1.438			0.804	0.572	< 0.0001	31 ^[b]
	30.012	−1.623		−2.192	0.988	0.168	< 0.0001	31 ^[b]
	29.940	−1.623	0.219	−2.215	0.990	0.185	< 0.0001	31 ^[b]
	28.659	−1.708			0.848	0.575	< 0.0001	31 ^[b]
	30.737	−1.132		−2.044	0.965	0.231	< 0.0001	31 ^[b]
MK(mor) ₂	30.685	−1.132	0.157	−2.061	0.962	0.230	< 0.0001	31 ^[b]
	29.476	−1.214			0.758	0.563	< 0.0001	31 ^[b]
	30.491			−2.248	0.658	0.649	< 0.0001	31 ^[b]
	30.102		−1.012	−1.240	0.875	0.232	< 0.0001	24 ^[c]
	30.140	−0.114	−0.990	−1.265	0.884	0.230	< 0.0001	24 ^[c]
MK(pipaz) ₂	30.356		−0.701	−1.636	0.884	0.179	< 0.0001	17 ^[d]
	30.151			−1.748	0.821	0.329	< 0.0001	17 ^[d]
	30.818	−0.171	−0.847	−1.576	0.868	0.262	< 0.0001	24 ^[c]
	30.765		−0.851	−1.547	0.852	0.269	< 0.0001	24 ^[c]
	30.997		−0.328	−2.284	0.814	0.471	< 0.0001	17 ^[d]
MK(pipazOH) ₂	30.901			−2.336	0.806	0.463	< 0.0001	17 ^[d]
	30.661	−1.250	0.016	−2.053	0.922	0.385	< 0.0001	31 ^[b]
	30.666	−1.250		−2.051	0.922	0.378	< 0.0001	31 ^[b]
	29.400	−1.330			0.748	0.636	< 0.0001	31 ^[b]

^[a] $v_{\max}$ value of water is excluded. ^[b] Probe was insoluble in water. ^[c] $v_{\max}$ values of triethylamine, chloroform, 1,1,2,2-tetrachloroethane, acetic acid, formamide, water, and 2,2,2-trifluoroethanol are excluded. ^[d] Solvents with $\alpha < 0$ are excluded. ^[e] $v_{\max}$ values of cyclohexane, benzonitrile, ethanol, acetic acid, formamide, ethane-1,2-diol, water, and 2,2,2-trifluoroethanol are excluded.

Multiple square analysis of the wavenumbers of the long-wavelength UV/Vis absorption bands of compounds **1a**, **1e**, **2b**, and **3** shows that the influence of the β term can be ignored, because of the smaller value of the coefficient **b** and the high error in this value. For **2d** and **2e**, the effect of β is more pronounced and significantly evident (see below).

Compounds **1a**, **1e**, **2a**, **2b**, **2c**, and **3** show solvatochromic properties as analysed by LSE relationships relating to pure **MK**. It should be emphasized at this point that the solvatochromic properties of **3** fit well into this concept, showing the importance of the individual chromophoric system for the respective solvatochromic property. The long-wavelength UV/Vis absorption maximum of BBP (**3**, Table 1, Figure 1) ranges from $\lambda_{\max} = 324$ nm in cyclohexane (CH) to $\lambda_{\max} = 383$ nm in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), corresponding to $\Delta\lambda = +59$ nm ($\Delta v_{\max} = -4750$ cm^{−1}). This compound thus shows more or less the same solvatochromic effect as **MK**.

The extent of the positive solvatochromic shift ($\Delta v_{\max}$) consists of two contributions originating from the influence of the dipolarity/polarizability (π^* term) and the hydrogen bond-donating capacity (α term) of the solvent. For all compounds studied, the influence of the dipolarity/polarizability (π^* term) on $\Delta v_{\max}$ dominates over that of the hydro-

gen bond-donating capacity (α term). Substituents with electronegative atoms (morpholino and acetoxy-piperazino) have little influence on **a**. Thus, the LSERs of **2c** and **2a** show lower **a** coefficient values than **1e** and **2b**. With an increasing Hammett σ_p^+ -substituent constant,^[16] an increase in **a** is to be expected.^[39] In general it seems that the specific acid-base interactions are difficult to quantify, because basicity parameters for the compounds used are still unavailable and difficult to determine. The value of the coefficient **a** decreases in the order: MK(NEt₂)₂ > MK(OAc)₂ > MK(pip)₂ > MK(pipOEt)₂ > MK(mor)₂ > MK(pipazOH)₂ > MK(pipaz)₂ (see Table 2).

Compounds **2d** and **2e** show ambiguous solvatochromic UV/Vis band shifts as functions of solvent polarity. The significant influence of the β term (HBA solvent property) compared to the HBD term of the solvent on the bathochromic shift of the UV/Vis band is really surprising. In strongly HBD solvents, such as water, acetic acid, and HFIP, a strong hypsochromic shift of the UV/Vis band is observed, which indicates that the positive mesomeric effect of the nitrogen atom at the aromatic system is suppressed. However, the basicity of the secondary nitrogen atom of the piperazine ring is greater than that of the tertiary nitrogen directly bonded to the aromatic system. It would therefore

be expected that a HBD solvent would interact preferentially with the secondary nitrogen atom of the piperazine ring, due to its greater basicity.

UV/Vis absorption spectra of **2d** in ethanolic solutions at different pH values are shown in Figure 2. At low pH, protonation takes place at the secondary nitrogen atoms and the UV/Vis absorption maximum is hypsochromically shifted. This shows that acid-base interactions at the secondary nitrogen atom have an influence on the tertiary nitrogen atom, probably by a through-space interaction from the nitrogen atom bonded at the aromatic system to the nitrogen atom in the piperazine 4-position, since only piperazine substituents with strongly basic nitrogen atoms show this effect.

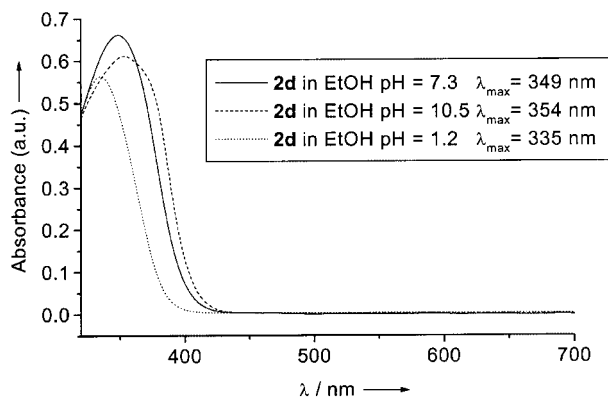
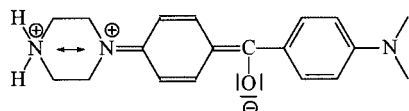
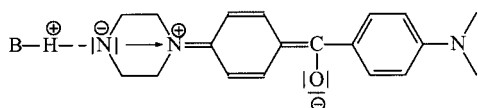


Figure 2. UV/Vis absorption spectra of MK(pipaz)₂ (**2d**) in ethanol (EtOH) at different pH values, with aqueous HCl (36%) and/or ethanolic NaOH used for adjusting the pH strength

With increasing pH, the solvatochromic UV/Vis band shifts bathochromically, even at pH > 7. This effect can be explained in terms of enhancement of the through-space interaction from the secondary nitrogen atom to the nitrogen atom at the aromatic system, which causes an increase in the positive mesomeric effect of the latter (Scheme 4).



(a) In acid medium, electrostatic repulsion between the two nitrogen atoms of the piperazine moiety take place.



(b) In basic medium, electrostatic attraction between the two nitrogen atoms of the piperazine moiety may occur.

Scheme 4. Proposed modification of the positive mesomeric effect by through-space interaction of piperazino-functionalized aromatic ketones

This effect is also observed for **2e**, but with a smaller influence of the β term on the extent of the bathochromic shift. This result shows, in accordance to our previous paper,^[7] that nitrogen-linked $-\text{CH}_2\text{CH}_2\text{OH}$ groups in the periphery of the probe govern an increase in the positive mesomeric effect when interacting with HBA solvents.

Because a range of specific interactions of the HBD capacity (α term) of the solvent with **2d** and **2e** cause opposite influences on the UV/Vis shift, no significant influence of the α term on ν_{max} for these compounds was found by multiple square analyses when utilizing Equation (1) and the Kamlet–Taft solvents parameter set.

X-Ray Crystal Structure Analysis of MK(pip)₂ (**2b**), MK(mor)₂ (**2c**), and BBP (**3**)

Crystallographic data for MK(pip)₂ (**2b**), MK(mor)₂ (**2c**), and BBP (**3**) are listed in Table 4 (Exp. Sect.). The solid-state structures of **2b**, **2c**, and **3** are shown in Figures 3–5,

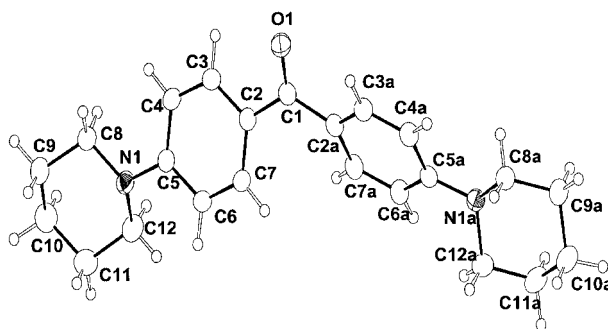


Figure 3. ZORTEP drawing (50% probability level) of MK(pip)₂ (**2b**); selected bond lengths [pm]: C(1)–O(1) 123.07(18), C(1)–C(2) 149.06(11), C(1)–C(2a) 149.07(11); selected bond angles [°]: O(1)–C(1)–C(2) 118.93(6), O(1)–C(1)–C(2a) 118.93(6), C(2)–C(1)–C(2a) 122.13(12); selected torsion angles [°]: O(1)–C(1)–C(2)–C(3) 19.79(9), O(1)–C(1)–C(2)–C(7) –155.69(8), C(2a)–C(1)–C(2)–C(3) –160.21(9), C(2a)–C(1)–C(2)–C(7) 24.31(8); for further details see Exp. Sect.

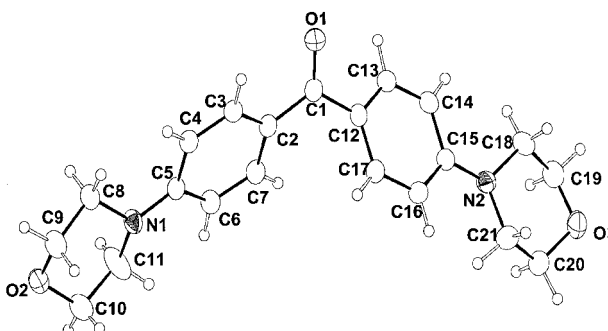


Figure 4. ZORTEP drawing (50% probability level) of MK(mor)₂ (**2c**); selected bond lengths [pm]: C(1)–O(1) 123.24(18), C(1)–C(2) 148.2(2), C(1)–C(12) 149.3(2); selected bond angles [°]: O(1)–C(1)–C(2) 120.66(15), O(1)–C(1)–C(12) 119.68(14), C(2)–C(1)–C(12) 119.65(12); selected torsion angles [°]: O(1)–C(1)–C(2)–C(3) –22.6(2), O(1)–C(1)–C(2)–C(7) 152.94(15), O(1)–C(1)–C(12)–C(13) –37.0(2), O(1)–C(1)–C(12)–C(17) 140.88(16); for further details see Exp. Sect.

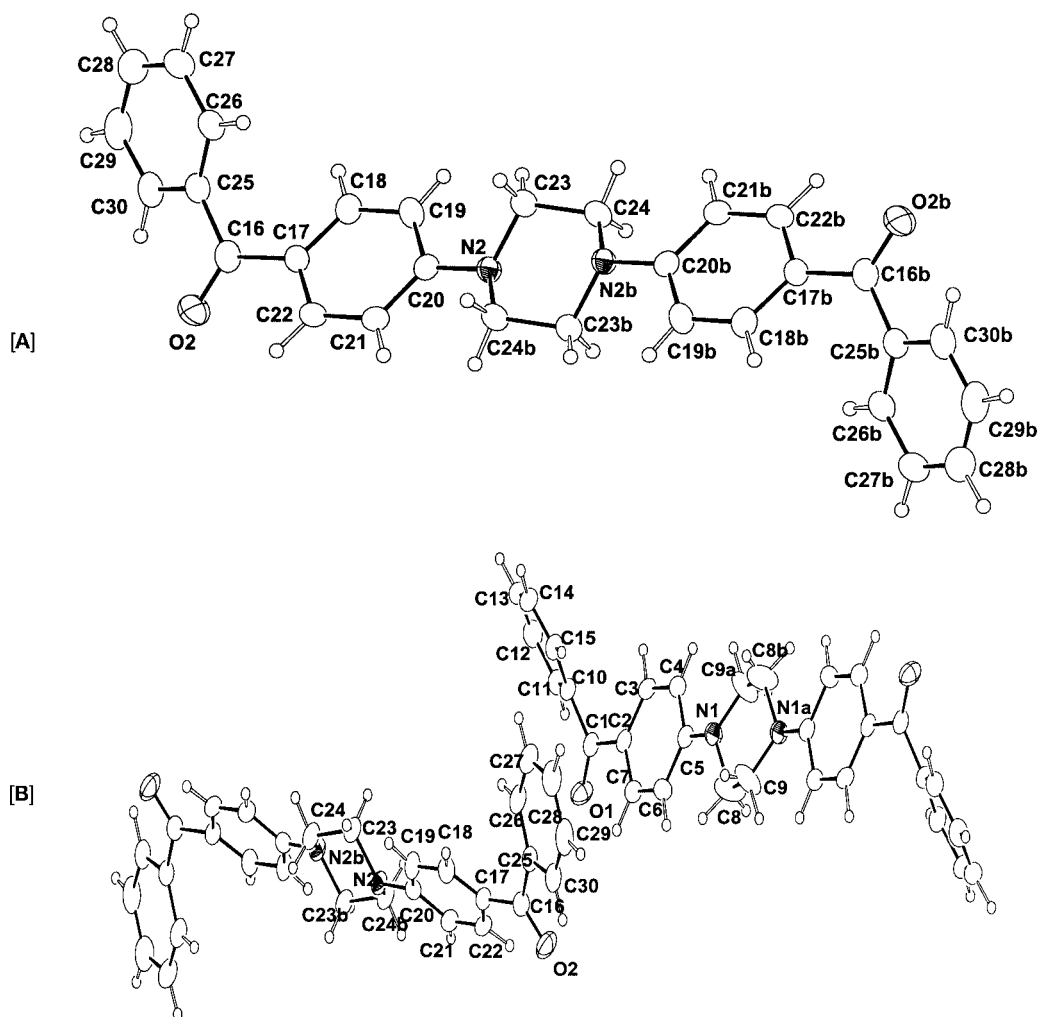


Figure 5. [A] ZORTEP drawing (50% probability level) of BBP (**3**); selected bond lengths [pm]: C(16)–O(2) 122.08(3), C(16)–C(17) 147.8(3), C(16)–C(25) 150.07(3); selected bond angles [°]: O(2)–C(16)–C(17) 120.6(2), O(2)–C(16)–C(25) 118.50(2), C(17)–C(16)–C(25) 120.9(2); selected torsion angles [°]: O(2)–C(16)–C(17)–C(18) 155.1(3), O(2)–C(16)–C(17)–C(22) –22.6(4), O(2)–C(16)–C(25)–C(26) 148.0(3), O(2)–C(16)–C(25)–C(30) –27.1(4), and [B] crystal structure (unit cell) of BBP **3**; for further details see Exp. Sect.

respectively. MK(pip)₂ (**2b**) crystallizes from ethyl acetate at 50 °C as yellow plates (Exp. Sect.) in the trigonal space group *P*3₁21, with *a* = 948.11(11), *b* = 948.11 (11), *c* = 1818.0(3) pm, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$, *V* = 1415.30(3)·10⁶ pm³ and *Z* = 3 (Figure 3). Molecule **2b** contains a twofold rotational axis of symmetry (symmetry code *y*, *x*, –*z*). The symmetry-generated atoms are indicated with the suffix “a”.

MK(mor)₂ (**2c**) crystallizes from saturated ethyl acetate solution at 50 °C as pale yellow rods in the orthorhombic space group *Pna*2₁, with *a* = 1259.90(2), *b* = 910.16(17), *c* = 1586.20(3) pm, $\alpha = \beta = \gamma = 90^\circ$, *V* = 1819.00(6)·10⁶ pm³ and *Z* = 4 (Figure 4).

BBP (**3**) crystallizes from a chloroform/ethyl acetate (1:2) mixture at 25 °C as yellow blocks in the triclinic space group *P*1̄, with *a* = 1034.0(2), *b* = 1079.9(2), *c* = 1127.2(2) pm, $\alpha = 72.062(4)^\circ$, $\beta = 73.361(4)^\circ$, $\gamma = 74.549(4)^\circ$, *V* = 1125.2(4)·10⁶ pm³ and *Z* = 2 (Figure 5, A).

The torsion angles for MK(pip)₂ are –1.49(14)° (C8–N1–C5–C4), 174.82(9)° (C8–N1–C5–C6), whereas

in MK(mor)₂ the values are 25.1(2)° (C8–N1–C5–C4), –158.60(15)° (C8–N1–C5–C6), 22.7(2)° (C18–N2–C15–C14), and –159.30(16)° (C18–N2–C15–C16). These data demonstrate that the terminal morpholino groups in **2c** are tilted more than the terminal piperidino groups in **2b** with respect to the central benzophenone moiety. This result also explains why the electron-donating density is greater for **2b** than for **2c**. In the solid state, the piperidino phenyl and the morpholino phenyl groups in **2b** and **2c** are twisted around the planar ketone substituents C2–C1–O1–C2a and C2–C1–O1–C12, respectively, in different ways, indicated by torsional angles of O1–C1–C2–C3 = 19.79(9)° and O1–C1–C2–C7 = –155.69(8)° in **2b**, and O1–C1–C2–C3 = –22.6(2)° and O1–C1–C12–C17 = 140.88(16)° in **2c**. This shows that the piperidino phenyl and the morpholino phenyl entities are bent with respect to the carbonyl plane. Hence, conformational differences between **2b** and **2c** in the solid state appear to be responsible for the differences in the UV/Vis absorption spectra of the two molecules.

The crystal packing diagram for BBP (**3**) is shown in Figure 5, B. The unit cell contains two geometrically similar, but crystallographically independent molecules, each with a crystallographically imposed centre of symmetry. Interatomic bond lengths and angles are identical within experimental limits. The two carbonyl groups of **3** are arranged *trans* to one another. It is interesting to note that the intermolecular aryl groups are not directly stacked over one another, but are closer to the carbonyl groups of the adjacent molecules.

UV/Vis Diffuse Reflectance Spectra of Crystal Powders of **1e**, **2a**, **2b**, **2c**, **2d**, **2e**, and **3**

Figure 6 shows the UV/Vis diffuse reflectance spectra of **1e**, **2b** and **2c**. The corresponding spectrum of **3**, for comparison, is already shown in Figure 1.

The three Michler's ketone derivatives (**1e**, **2b**, and **2c**) exhibit red-shifted UV/Vis absorption band maxima ($\lambda_{\max} \approx 400$ nm, $\nu_{\max} \approx 25000$ cm⁻¹) in the solid state, similarly to the UV/Vis spectra in solutions of a strongly polar solvent similar to HFIP. The results are summarized in Table 3.

However, the UV/Vis absorption bands are not symmetric. They show that different electronic transition occur in the solid state.

This result is probably due to the formation of aggregates, indicating strong dipolar interactions in the solid state. Among the other compounds, **2c** and **3** each show a clear

additional UV/Vis maximum, bathochromically shifted in its reflectance spectrum.

We believe that the position of the first absorption band at $\lambda_{\max} \approx 400$ nm in the solid state relates to the position of the UV/Vis absorption spectra in polar solvents. The second UV/Vis band at $\lambda_{\max} \approx 450$ – 500 nm is significantly red-shifted with respect to the first band. This UV/Vis absorption band is probably attributable to the presence of strong intermolecular π - π stacking interactions between the aromatic moieties in the solid state, as suggested by the crystal structure analyses. Charge-transfer transitions may also contribute to this new UV/Vis absorption band.

Relationship between Solvatochromic and Structural Data

From Table 3 it follows that the two MK homomorphs MK(pip)₂ and MK(mor)₂ show molar volume (V/Z) values of ca. 471.77 and 454.75 pm³: a significantly smaller molecular density in **2c** than in **2b**. Comparison between the observed values of the densities of the different packings (Table 4) and the positions of the UV/Vis absorption band maxima (Table 3) shows a clear correlation: the denser the packing, the more strongly bathochromically shifted the UV/Vis absorption band of the compound in the solid state.

Interaction between the carbonyl groups of **3** and the aromatic ring of its neighbouring molecule may give rise to charge-transfer transitions. For deeper understanding of the crystallochromic effects, more theoretical and angle-dependent optical investigations with well defined single crystals are required.

Conclusion

The influence of polar and HBD and HBA functionalities (e.g. morpholino, piperidino, piperazino, and *N*-substituted piperazines) as *para*-substituents at the peripheries of aromatic amino ketones of the Michler's ketone type, and also of a piperazino-bridged diketo derivative, have been studied and have provided detailed information on the solvatochromic properties of polar compounds in relation to structural features. In organic solvents, single-molecule solvation is observed, which can readily be explained in terms of empirically derived LSERs by use of the Kamlet–Taft solvent parameter set. The influence of the solvent on the

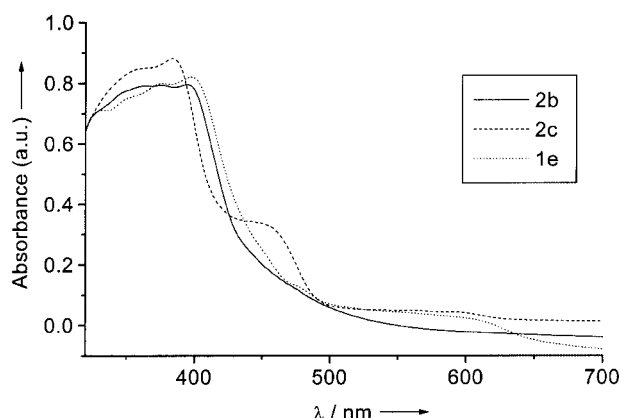


Figure 6. UV/Vis reflectance spectra of MK(NEt₂)₂ (**1e**), MK(pip)₂ (**2b**) and MK(mor)₂ (**2c**) as crystal powders in the solid state

Table 3. UV/Vis reflectance absorption maxima (uncorrected) of the crystal powders of seven aromatic amino ketones

Compound	$\lambda_{\max}(1)$ /nm	$\lambda_{\max}(2)$ /nm	$I_1/I_2^{[a]}$	Comment
MK(NEt ₂) ₂ (1e)	377	397	0.97	$\lambda_{\max}(2)$ small shoulder
MK(pipOEt) ₂ (2a)	365			
MK(pip) ₂ (2b)	375	394	1.00	
MK(mor) ₂ (2c)	384	449	2.61	$\lambda_{\max}(2)$ appears as shoulder
MK(pipaz) ₂ (2d)	366			
MK(pipazOH) ₂ (2e)	355			
BBP(3)	375	469	2.11	$\lambda_{\max}(2)$ is poorly resolved

[a] Intensity ratio of the two UV/Vis absorption bands [at $\lambda_{\max}(1)$ and $\lambda_{\max}(2)$].

Table 4. Crystal data, details of data collection, and structure analysis of MK(pip)₂ (**2b**), MK(mor)₂ (**2c**), and BBP (**3**)

	MK(pip) ₂ (2b)	MK(mor) ₂ (2c)	BBP (3)
Crystal colour, shape	yellow, plate	light yellow, rod	yellow, block
Crystal size [mm]	1.20×1.00×0.30	1.00×0.40×0.30	0.40×0.20×0.10
Empirical formula	C ₂₃ H ₂₈ N ₂ O	C ₂₁ H ₂₄ N ₂ O ₃	C ₃₀ H ₂₆ N ₂ O ₂
Chemical formula	C ₂₃ H ₂₈ N ₂ O	C ₂₁ H ₂₄ N ₂ O ₃	C ₃₀ H ₂₆ N ₂ O ₂
Molecular weight	348.47	352.42	446.53
Crystal system	trigonal	orthorhombic	triclinic
Space group	<i>P</i> 3 ₁ 21	<i>Pna</i> 2 ₁	<i>P</i> 1̄
Unit cell dimensions [pm], angles [°]	<i>a</i> = 948.11(11) <i>b</i> = 948.11(11) <i>c</i> = 1818.0(3) α = 90 β = 90 γ = 120	<i>a</i> = 1259.9(2) <i>b</i> = 910.16(17) <i>c</i> = 1586.2(3) α = 90 β = 90 γ = 90	<i>a</i> = 1034.0(2) <i>b</i> = 1079.9(2) <i>c</i> = 1127.2(2) α = 72.062(4) β = 73.361(4) γ = 74.549(4)
Volume [10 ⁶ pm ³]	1415.3(3)	1819.0(6)	1125.2(4)
<i>Z</i>	3	4	2
Density (calculated) [g cm ⁻³]	1.227	1.287	1.318
Linear absorption coefficient [mm ⁻¹]	0.075	0.086 mm ⁻¹	0.083 mm ⁻¹
Scan method	ω scans		
Absorption correction	empirical		
Max./min. transmission	0.9779/0.9154	0.9745/0.9185	0.9918/0.9677
Measured reflections	11667	13320	9293
Independent reflections	2776	3716	6229
Observed reflections [<i>I</i> ≥ 2 σ (<i>I</i>)]	2464	3206	2329
<i>R</i> (int)	0.0247	0.0318	0.0521
θ range for data collection [°]	2.48–30.85	2.58–30.85	1.95–30.92
Completeness to maximum θ [%]	95.2	94.5	87.4
Index ranges	–10 ≤ <i>h</i> ≤ 13, –13 ≤ <i>k</i> ≤ 9, –25 ≤ <i>l</i> ≤ 22	–18 ≤ <i>h</i> ≤ 17, –13 ≤ <i>k</i> ≤ 12, –9 ≤ <i>l</i> ≤ 22	–14 ≤ <i>h</i> ≤ 12, –14 ≤ <i>k</i> ≤ 13, –12 ≤ <i>l</i> ≤ 15
Final <i>R</i> indices <i>R</i> ₁ / <i>wR</i> ₂ [<i>I</i> ≥ 2 σ (<i>I</i>)]	0.0345/0.0884	0.0352/0.0890	0.0634/0.1046
<i>R</i> indices <i>R</i> ₁ / <i>wR</i> ₂ (all data)	0.0401/0.0908	0.0444/0.0933	0.2015/0.1430
Maximum δ/σ	0.010	0.010	0.028
Max./min. e-density [10 ⁻⁶ e·pm ⁻³]	0.165/–0.205	0.190/–0.191	0.209/–0.255

position of the solvatochromic UV/Vis absorption band depends on the nature (polarity, basicity, and steric requirements) of the (+M) substituent. The stronger the (+M) effect of the substituent, the larger the extent of the solvatochromic effect induced by the HBD capacity of the solvent. The introduction of basic moieties such as piperazine causes a worsening of the LSERs, due to competing acid–base interactions. This sometimes makes interpretation of the solvatochromism ambiguous.

If the crystals of the compounds studied are densely packed, then a new UV/Vis band at about $\lambda = 450$ nm is observed. These effects are perhaps attributable to charge-transfer transitions due to π stacking and induced dipole–dipole interactions. These results merit deeper theoretical and extended optical studies.

Experimental Section

Materials: Solvents from Merck, Fluka, Lancaster and Aldrich were distilled over appropriate drying agents prior to use. 4,4'-Bis(diethylamino)benzophenone [MK(NEt₂)₂, **1e**] from Merck, stated purity > 99% was crystallized twice from ethanol before use. The synthesis of 4'-[bis(2-acetoxyethyl)amino]-4-(dimethylamino)-benzophenone [MK(OAc)₂, **1a**] was described previously.^[7]

Spectral Measurement: The UV/Vis absorption spectra were obtained with the aid of a UV/Vis spectrometer (MCS 400 diode-array spectrometer from Carl Zeiss, Jena), connected to an immersion cell (TSM 5) by glass-fibre optics. NMR measurements were recorded at 20 °C on a Varian Gemini 300 FT NMR spectrometer operating at 300 MHz for ¹H and 75 MHz for ¹³C. The signals of the solvents (CDCl₃ or CD₃OD) were used as internal standards. ES-MS spectra were obtained with a Mariner system 5229 spectrometer (Applied Biosystems) and the EI-MS spectrum with a MAT 95XL.

Correlation Analysis: Multiple regression analysis was performed with the Origin 5.0 statistical programs.

Structure Determination: Crystal structures of MK(pip)₂ (**2b**), MK(mor)₂ (**2c**), and BBP were determined by single-crystal X-ray diffraction methods. Data collection for these compounds were performed at –100 °C with graphite monochromatized Mo-*K*_α ($\lambda = 71.073$ pm) radiation on a Bruker AXS SMART 1KCCD area detector. Complete data collection parameters and details of the structure solution and refinement are given in Table 4.

Further details of the crystal structure investigation (without structural factors) are available: CCDC-193643 (**2b**), CCDC-193644 (**2c**), and CCDC-193645 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cam-

bridge CB2 1EZ, UK; Fax: (internat.) +44–1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

The unit cells were determined with the program SMART.^[40] For data integration and refinement, the unit cell program SAINT^[40] was used. The space group was determined with the aid of the programs XPRED^[40] for **2b** and **2c**, and ABSEN^[41] for **3**, and the empirical absorption correction was performed with SADABS.^[42] The structures were solved by direct methods with the programs SHELX97^[43] for **2b** and **2c**, and SIR97^[44] for **3**. The structure refinement by least-square methods based on F^2 was carried out with SHELX97.^[43]

All non-hydrogen atoms were fully refined in the calculated positions when possible; the hydrogen atoms were taken from the electron density difference map and refined freely in both their position and their thermal parameters.

The plots of the molecular structures were made with the programs ZORTEP^[45] and SCHAKAL97.^[46]

4,4'-Bis(4-ethoxycarbonylpiperazino)benzophenone [MK(pipOEt)₂, 2a]: 4,4'-Difluorobenzophenone (4.36 g, 0.02 mol) and ethyl *N*-piperazine-1-carboxylate (12.66 g, 0.08 mol) were stirred under argon in dimethyl sulfoxide (25 mL) at 140 °C for 40 h. The resulted reaction mixture was poured into ice water. The crude material was filtered and washed with water, and then crystallized from ethyl acetate to give **2a** (5.93 g, 60%) as a pale yellowish powder with m.p. 158 °C. ¹H NMR (CDCl₃): δ = 7.72 (d, J = 8.69 Hz, 4 H, ArH-2,6,2',6'), 6.88 (d, J = 8.69 Hz, 4 H, ArH-3,5,3',5'), 4.16 (q, J = 7.11 Hz, 4 H, COOCH₂), 3.62 (t, J = 4.90 Hz, 8 H, CH₂NCOO), 3.30 (t, J = 4.90 Hz, 8 H, CH₂NPh), 1.27 (t, J = 7.11 Hz, 6 H, CH₃) ppm. ¹³C NMR (CDCl₃): δ = 194.15 (C=O), 155.79 (C=O ester), 153.69 (ArC-4,4'), 132.36 (ArC-2,6,2',6'), 129.27 (ArC-1,1'), 114.32 (ArC-3,5,3',5'), 61.94 (OCH₂), 48.00 (CH₂NCOO), 43.63 (CH₂NPh), 15.08 (CH₃) ppm. C₂₇H₃₄N₄O₅ (494): calcd. C 65.57, H 6.93, N 11.33; found C 65.65, H 6.84, N 11.14.

4,4'-Bis(piperidino)benzophenone [MK(pip)₂, 2b]: 4,4'-Difluorobenzophenone (21.82 g, 0.10 mol) and piperidine (34.06 g, 0.4 mol) were heated at reflux under argon in tetramethylene sulfone (100 mL) at 140 °C for 30 h. After cooling to room temperature, the solution was poured into cold water (2 dm³). The resulting solid was filtered, washed thoroughly with 50 mL of water, dried under vacuum, and recrystallized from ethyl acetate to afford 22.62 g (65%) of MK(pip)₂ (**2b**) as a pale yellow solid crystals with m.p. 152 °C (ref.^[8] 140–142 °C from acetone). ¹H NMR (CDCl₃): δ = 7.76 (d, J = 8.69 Hz, 4 H, ArH-2,6,2',6'), 6.92 (d, J = 8.69 Hz, 4 H, ArH-3,5,3',5'), 3.36 (t, J = 5.37 Hz, 8 H, NCH₂), 1.72 (m, 12 H, NCH₂CH₂CH₂), 1.27 (t, J = 7.11 Hz, 6 H, CH₃) ppm. ¹³C NMR (CDCl₃): δ = 194.23 (C=O), 154.26 (ArC-4,4'), 132.46 (ArC-2,6,2',6'), 128.18 (ArC-1,1'), 113.87 (ArC-3,5,3',5'), 49.33 (NCH₂), 25.84 (NCH₂CH₂), 24.77 (NCH₂CH₂CH₂) ppm. C₂₃H₂₈N₂O (348): calcd. C 79.27, H 8.10, N 8.04; found C 79.19, H 7.96, N 7.96.

4,4'-Bis(morpholino)benzophenone [MK(mor)₂, 2c]: MK(mor)₂ (**2c**) was prepared in a way similar to that described above, from 4,4'-difluorobenzophenone (21.82 g, 0.10 mol) and morpholine (34.85 g, 0.4 mol). Crystallization from ethyl acetate at 50 °C afforded MK(mor)₂ (**2c**, 28.16 g, 80%) as cream needles with m.p. 171 °C (ref.^[8] 162–164 °C from ethanol). ¹H NMR (CDCl₃): δ = 7.69 (d, J = 8.85 Hz, 4 H, ArH-2,6,2',6'), 6.82 (d, J = 8.85 Hz, 4 H, ArH-3,5,3',5'), 3.79 (t, J = 4.90 Hz, 8 H, OCH₂), 3.23 (t, J = 4.90 Hz, 8 H, NCH₂) ppm. ¹³C NMR (CDCl₃): δ = 194.38 (C=O), 154.01 (ArC-4,4'), 132.39 (ArC-2,6,2',6'), 129.38 (ArC-1,1'),

113.76 (ArC-3,5,3',5'), 67.04 (OCH₂), 48.24 (NCH₂) ppm. C₂₁H₂₄N₂O₃ (352): calcd. C 71.57, H 6.86, N 7.95; found C 71.08, H 6.68, N 7.94.

4,4'-Bis(piperazino)benzophenone [MK(pipaz)₂, 2d]: 4,4'-Difluorobenzophenone (8.73 g, 0.04 mol) and piperazine (34.46 g, 0.4 mol) in dimethyl sulfoxide (50 mL) were stirred under argon at 140 °C for 40 h. After cooling to room temperature, the mixture was poured into ice-water. The precipitate was filtered off, washed with water and crystallized at 70 °C from ethanol to afford MK(pipaz)₂ (**2d**, 7.35 g, 52.5%) as a pale yellow powder with m.p. 170–172 °C. ¹H NMR (CD₃OD): δ = 7.74 (d, J = 9.00 Hz, 4 H, ArH-2,6,2',6'), 7.10 (d, J = 9.00 Hz, 4 H, ArH-3,5,3',5'), 3.62 (t, J = 5.21 Hz, 8 H, NCH₂), 3.31 (t, J = 5.21 Hz, 8 H, CH₂NH) ppm. ¹³C NMR (CDCl₃): δ = 196.77 (C=O), 154.97 (ArC-4,4'), 133.54 (ArC-2,6,2',6'), 130.76 (ArC-1,1'), 115.95 (ArC-3,5,3',5'), 46.77 (NCH₂), 44.80 (CH₂NH) ppm. C₂₁H₂₆N₄O (350): MS (EI), m/z (relative abundance, %): 351 (4) [M⁺ + 1], 350 (12) [M⁺], 308 (16), 256 (22), 129 (20), 97 (16), 83 (16), 73 (26), 57 (26), 45 (28), 31 (36).

4,4'-Bis[4-(2-hydroxyethyl)piperazino]benzophenone [MK(pipaz-OH)₂, 2e]: Piperazin-2-ylethanol (6.51 g, 50 mmol) was added to a mixture of 4,4'-difluorobenzophenone (5.46 g, 25 mmol) and potassium carbonate (6.9 g, 50 mmol) in dry dimethyl sulfoxide (50 mL). After heating to 140 °C for 48 h, the solution was cooled to room temperature, and poured into water (1 L). The precipitate was filtered off, and washed several times with water, dried, and recrystallized from ethanol to afford **2e** (7.80 g, 71.2%) as a fine, pale yellow powder with m.p. 115–117 °C. ¹H NMR ([D₆]DMSO): δ = 7.62 (d, J = 8.37 Hz, 4 H, ArH-2,6,2',6'), 7.00 (d, J = 8.37 Hz, 4 H, ArH-3,5,3',5'), 3.60 (t, J = 5.5 Hz, 4 H, CH₂O), 3.28 (t, J = 5.5 Hz, 4 H, NCH₂CH₂O), 2.44–2.60 (m, 16 H, NCH₂CH₂N) ppm. ¹³C NMR ([D₆]DMSO): δ = 192.67 (C=O), 153.59 (ArC-4,4'), 131.78 (ArC-2,6,2',6'), 127.48 (ArC-1,1'), 115.51 (ArC-3,5,3',5'), 60.56 (CH₂O), 58.92 (CH₂CH₂O), 53.27 (NCH₂), 46.87 (NCH₂CH₂NH) ppm. C₂₅H₃₄N₄O₃ (438) MS (ESI), m/z = 439 [M⁺ + 1].

1,4-Bis(4-benzoylphenyl)piperazine (BBP, 3): 4-Fluorobenzophenone (2.00 g, 10 mmol), potassium carbonate (1.38 g, 10 mmol), and anhydrous piperazine (0.43 g, 5 mmol) in dimethyl sulfoxide (20 mL) were heated at 140 °C for 48 h. After cooling to room temperature, the crude reaction mixture was taken up in water (400 mL), and the precipitate formed was filtered off, washed several times with water, dried, and purified by column chromatography (silica gel, chloroform/ethyl acetate, 2:1), affording **3** (1.78 g, 80.0%) as yellow crystals with m.p. 213 °C. ¹H NMR (CDCl₃): δ = 7.86 (d, J = 8.69 Hz, 4 H, ArH-2,6,2',6'), 7.78 (d, J = 8.69 Hz, 4 H, ArH-8,12,8',12'), 7.46–7.58 (m, 6 H, ArH-9,10,11,9',10',11'), 6.96 (d, J = 8.85 Hz, 4 H, ArH-3,5,3',5'), 3.60 (s, 8 H, NCH₂) ppm. ¹³C NMR (CDCl₃): δ = 195.57 (C=O), 153.74 (ArC-4,4'), 139.12 (ArC-1,1'), 132.96 (ArC-2,6,2',6'), 131.98 (ArC-7,7'), 129.99 (ArC-8,12,8',12'), 128.54 (ArC-9,11,9',11'), 128.14 (ArC-10,10'), 113.74 (ArC-3,5,3',5'), 47.38 (NCH₂) ppm. C₃₀H₂₆N₂O₂ (446) MS (ESI), m/z = 447 [M⁺ + 1].

Acknowledgments

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