Molecular complexes. Part 12.[1] Dimeric toluene, torsional vibrations, dipoles and isomeric complexes in ^{1}H NMR studies of weak arene complexes. Temperature dependence of CH signals

Helmut Stamm,*[a] Hanns-Otto Strumm,[a] Karl-Heinz Loebel,[a] Hannelore Jäckel,[a] Ulrich Hoffmanns,[a] Sabine Bethke[b] and Gerhard Schilling[b]

[a] *Pharmazeutisch-Chemisches Institut, University of Heidelberg, Neuenheimer Feld 364, D-69120 Heidelberg, Germany*
[b] *Organisch-Chemisches Institut, University of Heidelberg, Neuenheimer Feld 270, D-69120 Heidelberg, Germany*

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The refined (AUS concept, CCl_4, external ref.) ^{1}H NMR method provided association constants *K* and approximate complex shifts *IK* for stacking complexes of aromatic hydrocarbons D with A when A is 4-nitrobenzaldehyde (**1**) or is related to **1**. D covers the benzene ring of A but torsionally vibrating substituents in A influence topology and *K*. In the absence of D, vibrations of A can be slowed by low temperatures making A signals go downfield in accord with an increased planarity of A. Vibration of CHO (a dipole) in complexes of **1** with benzene **B** or toluene **T** is made non-symmetric by interactions with the quadrupole of D. The large naphthalene (**N**) hinders vibrations thus enhancing the contact interface by a more planar **1** whose intramolecular deshielding of protons is increased providing small *IK* values. Aldehyde **1** forms complexes both with **T** and with its stacking dimer $\mathbf{T}_2$ since *IK* values for **1**–**T** are significantly greater than for **1**–**B**. Complexing with $\mathbf{T}_2$ is not found when the molecular dimensions of A allow a dipole–dipole interaction with **T** as in face-to-face complexes of 1-ethyltheobromine † or of 1-chloro-2,4-dinitrobenzene (**7**). Different protons give slightly different values of *K* for **7**–**T** and this points to an isomeric edge-on complex with both **T** and $\mathbf{T}_2$ where *K* for the two edge-on protons (shortest distance to D) is the sum of the binary *K* and the small *K* for the the ternary (**7** + $\mathbf{T}_2$) complex. Compound **7** and 1,3,5-trimethylbenzene show some of the effect described for **1**–**N**.

Introduction

Investigations of weak complexes can provide reliable results when complexation effects predominate. Several problems are avoided with CCl_4 as solvent and *M* as concentration unit.[2] Reports from this laboratory using the refined ^{1}H NMR shift method (AUS concept, external reference, see below)[3,4] showed that aromatic hydrocarbons D and several species A form (usually) face-to-face complexes AD whose topologies are controlled by distribution of partial charges in A (polar effects) and whose association constants *K* (0.08–3.55 M^{-1}) increase with the resulting contact interface (roughly a linear correlation with log *K*)[5] indicating an essential influence of dispersion forces. When the interface and the latter are too small with a small A the polar effect can dominate making the stacking topology change to a T-shaped AD with dipole–quadrupole interaction.[2] Charge transfer (CT) contributions were not detected or could even be excluded.[2] This work centred on caffeine **C** (Fig. 1) and related planar compounds with a fixed conformation. A was selected such that two to four independent ^{1}H NMR signals allowed separate data reductions whose congruence in *K* serves to check on both the underlying model and the 1 : 1 stoichiometry.

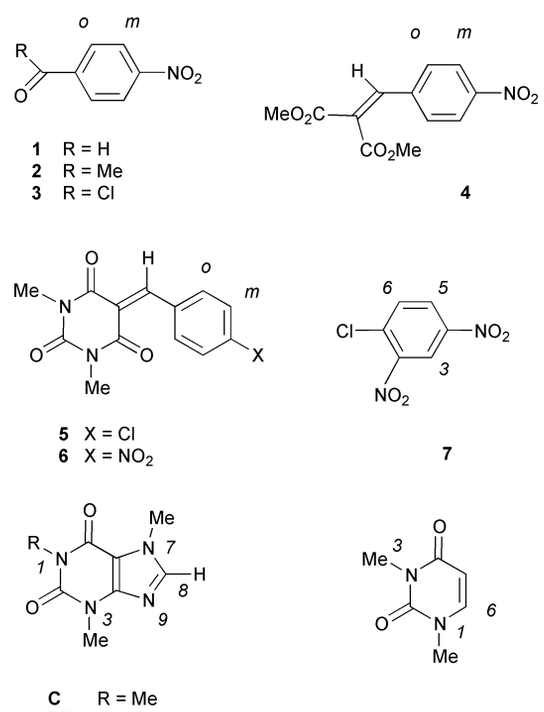

Fig. 1 Structures of A; numbering and labels of proton sites.

Method

Formation of AD is recognized from the shielding of A protons by the ring current effect of the complexing D. The AUS (additional unspecific shielding)[3,4] concept distinguishes complexation shifts and collision shifts and may be compared with the contact CT absorption of Orgel and Mulliken in electronic

† The IUPAC name for theobromine is 3,7-dihydro-3,7-dimethyl-1*H*-purine-2,6-dione.

spectra of CT complexes.[6] Non-specific shielding of A protons by excess D (total concentration $[D_0]$) is taken into account by linear corrections a_1 $[D_0]$ for A and a_2 $[D_0]$ for AD which provide incorrect results with one of the common internal references whose shift depends on $[D_0]$ in a non-linear relation.[7] The change of magnetic susceptibility with $[D_0]$ is considered by b $[D_0]$.[5] Then, eqns. (1)–(5) replace the well-known Foster–

$$(\Delta_0 - m_2[D_0])/[D_0] = -K(\Delta_0 - m_2[D_0]) + Icpt \quad (1)$$

$$Icpt = KIK = K[\Delta_{AD,00} + (m_1 - m_2)K^{-1}] \quad (2)$$

$$m_1 = a_1 + b \quad (3)$$

$$m_2 = a_2 + b \quad (4)$$

$$IK = Icpt/K \quad (5)$$

Fyfe relation $\Delta_0/[D_0] = -K\Delta_0 + K\Delta_{AD}$;[3,8] definition of Δ_0 and Δ_{AD} follows, K is defined above. Total A concentration $[A_0]$ is advantageously held constant while $[D_0]$ ($[D_0] >> [A_0]$) in an experimental series of n solutions is evenly distributed over the largest possible range. The value of n should be large, but not so high as to prevent the completion of a series within one day. Δ_0 is the difference between chemical shifts of A in the absence of D and in the presence of $[D_0]$. IK is an approximation for $\Delta_{AD} = (\delta_A - \delta_{AD})$ of the classical model or, more precisely, $\Delta_{AD,00}$ of the AUS model.[3] IK and m_2 are obtained for each signal of A; m_1 usually remains unknown but resembles m_2 in size. IK depends on D and on distances in AD thus enabling reliable conclusions on the topology of an AD.

This refined model is of prime importance for weak complexes. One of the results in this paper demonstrates the magnitude of specific and non-specific effects. With $K = 0.14$ M^{-1}, $10^2IK = 172$ ppm and $10^2m_2 = 4.7$ ppm M^{-1} the latter consists of $10^2a_2 = 3.4$ ppm M^{-1} and $10^2b_{benzene} = 1.3$ ppm M^{-1} while Δ_0 contains 68–83% specific effects. Δ_0 for another proton with $10^2IK = 201$ ppm and $10^2m_2 = 8.0$ ppm M^{-1} contains 59–77% specific effects. With increasing K and large $\Delta_{AD,00}$ complexation effects predominate more and more until non-specific shielding can be ignored.[5,9] The saturation fraction $SF = [AD]/[A_0]$ evenly covers at best a broad range between 0.2 and 0.8 (Person and Deranleau).[10,11] For further details and computer programs CA-AUS or Sc-AUS (more sensitive to experimental errors) see refs. 2–4. CA-AUS is based on the Cresswell–Allred method,[12] Sc-AUS on the Scatchard–Foster–Fyfe method.[8] Both programs correct the approximation $[D] = [D_0]$ in eqn. (1). The soundness of the basic idea follows from (amongst other evidence) a linear shift dependence $m_1[D_0]$ for more than 30 arenes and substituted arenes when the probe signal is not influenced ($\Delta_{AD,00} = 0$, $a_2 = 0$) by complexation.[13] The reliability of the IK values allows, for the first time, the consideration of torsional vibrations in A. It will be shown here that the AUS method can even detect isomeric complexes which usually cannot be distinguished or recognized because the experimental K is the sum of all 1 : 1 constants.[14] Without AUS corrections, with internal reference and concentrations in moles per kg of solution, K of hexamethylbenzene complexes with **1** and **2** (Fig. 1) was found to depend on the proton measured.[15]

Results

Results obtained from compounds **1**–**5** and **7** (Fig. 1) are presented in Tables 1 and 2 where **B** stands for benzene (C_6D_6), **T** for toluene (C_7D_8), **M** for 1,3,5-trimethylbenzene (mesitylene, not deuterated) and **N** for naphthalene ($C_{10}D_8$). The congruence in K is always good. Parameters (Table 1) of the **B** complex **1–B** of **1** (Fig. 1) are taken from the literature.[4]

Only CA-AUS results are reported. Sc-AUS results did not significantly deviate apart from one case (see **2–B** in Table 1). Values of m_2 are reported but not discussed. Temperature dependence of chemical shifts for CH signals is given either in the text when required to support proposed torsional vibrations or in a separate section on thermal influences of vibrations and other factors.

Discussion

Benzene complexes of 1–3; torsional vibrations and ^{1}H NMR

The CHO proton of **1** was replaced (**2**, **3**, Fig. 1) by Me and Cl. With **3** the electron-withdrawing power of RC=O is substantially increased leading to a stronger polar effect in the complexation with **B**. In AM1 computations the group partial charge of the C_6H_4 moiety increases in the sequence **1** < **2** < **3**. The corresponding influence on K (Table 1) is found for complexes **2–B** and **3–B** but both have a smaller K than **1–B**, pointing to steric hindrance when R ≠ H. Steric repulsion of the complexing **B** is impossible with completely planar **2** and **3**. Aromatic aldehydes and other conjugated aromatics have a planar conformation but they are not forced to strict planarity. Torsional vibrations of substituents are easily excited and their amplitudes have the longest lifetimes of all vibrational conformations. In the mean, such vibrations make R as well as the oxygen atoms of NO_2 and RC=O in **2** and **3** protrude from the molecular face even at ordinary temperatures (30 °C for Tables 1 and 2). This changes the effects of intramolecular anisotropies and resonances making the proton signals in **1**, **2** and **3** go upfield relative to complete planarity. Resonance effects on aromatic protons decrease with decreasing planarity. Deshielding of protons in a substituent (*e.g.* CHO of **1**) by the intramolecular ring current effect is lessened when such protons leave the aromatic plane. Aromatic protons next to an anisotropic substituent are also more shielded at ordinary temperatures due to a decreased anisotropy effect; such shifts will be comparatively large with a short distance between proton and anisotropic group. Thus, the experimental chemical shifts of compounds **1**–**3** cannot be assigned to the really planar molecules undergoing only zero point vibrations. Torsional vibrations precede rotations and change into rotations with sufficient thermal energy. Both require comparatively small energies for **1**–**3** since resonance stabilization is small due to pull–pull substitution. For CHO rotations in benzaldehydes the influence of resonance is known, the barrier is 33 kJ mol^{-1} for benzaldehyde.[16] Torsional vibrations will require a small fraction of this energy. They will depend on the temperature such that the chemical shifts go downfield on cooling. Further support for this reasoning comes from abnormal parameters for the **N** complex of **1** as discussed later.

In CCl_4 at −15 °C the chemical shifts (in ppm throughout the paper) of **1** were found downfield by 0.0115 for CHO, 0.040 for the *ortho* protons and 0.044 for the *meta* protons relative to +25 °C; −15 °C is the limit for CCl_4. For other solvents see separate section. Dilution (0.066 $M \longrightarrow 0.008$ M) experiments with **1** in CD_3COCD_3 provided at 25 °C (at −80 °C) downfield shifts of 0.0018 (0.0042) for CHO, 0.0024 (0.0055) for *ortho* and 0.0026 (0.0061) for *meta* protons relative to +25 °C. This concentration dependence may be ascribed to a kind of AUS effect where **1** is both A and D. The greater shifts at −80 °C result then from an increase of the total molecular anisotropy.

One may conclude from the IK values of **1–B** that **B** in the mean is face-to-face placed over a point (complex centre) in **1** about equidistant to the protons in CHO and in an *ortho* position but with a larger distance to the *meta* protons in accord with a repulsion of **B** by the vibrating nitro group. This repulsion may not be purely steric in nature. The negative charges of the oxygen atoms will also repel **B** in analogy to the rather strong repulsion of **B** by carbonyl oxygen atoms of planar A molecules.[5,17] IK values for the *ortho* protons are

Table 1 Complex parameters of **1**–**5** from *m* experimental series

				10^2IK (max. deviation)/ppm 10^2m_2 (max. deviation)/ppm M^{-1}			
A–D	*m*	SF	K/M^{-1}	O=CR (**1**–**3**) C=CH (**4**–**5**)	*ortho*	*meta*	Me1 [a] Me2 [a]
1–B	1		0.125	152.4 (0.2) 5.6	157.9 (0.3) 6.8	123.2 (0.3) 6.8	
2–B	2	0.07–0.50	0.088 ± 0.004	150.8 (7.7) [b] 5.9 (0.2)	157.6 (1.0) 5.6 (0)	138.1 (0.9) 5.2 (0.1)	
3–B	1	0.18–0.51	0.103		155.0 6.9	170.8 6.0	
4–B [c]	2	0.06–0.46	0.085 ± 0.001	85.7 (0.3) 3.8 (0)	166.2 (2.4) 4.9 (0)	131.4 (1.9) 5.7 (0.2)	Unreliable parameters [d]
5–B	2	0.12–0.51	0.099 ± 0.002	92.6 (0.1) 2.5 (0.1)	99.5 (4.3) 5.2 (0.2)	60.8 (5.7) 6.7 (0.2)	79.6 (0.9) 5.2 (0.1) 67.3 (0.1) 4.1 (0.1)
1–T	2	0.05–0.47	0.107 ± 0.002	207.2 (0.3) 4.1 (0)	203.9 (0.1) 5.7 (0)	171.9 (3.1) 5.7 (0.1)	
1–N	3	0.13–0.46	0.415 ± 0.004	143.4 (1.1) 13.2 (0.6)	160.9 (0.6) 17.4 (0.2)	128.7 (3.6) 15.0 (0.6)	

[a] Me1 high field, Me2 low field line. [b] Sc-AUS provided 145.9 (3.9). [c] One line of the *ortho* doublet of one series had too many overlapping signals and was not included in the calculations. [d] Unreliable parameters (sequence *K*, 10^2IK, 10^2m_2) as follows. Me1: 0.042, 144–149, 5.2; Me2: 0.037–0.038, 196–202, 5.2–5.4.

Table 2 Complex parameters of **7** from *m* experimental series

				10^2IK (max deviation)/ppm 10^2m_2 (max deviation)/ppm M^{-1}		
A–D	*m*	SF	K/M^{-1}	3-H	5-H	6-H
7–B	2	0.08–0.60	0.141 ± 0.002	171.9 (3.6) 4.7 (0.3)	198.6 (5.3) 6.2 (0.4)	200.6 (0.9) 8.0 (0.2)
7–T total		0.11–0.61	0.181 ± 0.004	162.6 (0.8) 5.4 (0.1)	179.7 (6.7) 7.2 (0.3)	178.7 (1.8) 9.1 (0.1)
5-H + 6-H			0.183 ± 0.001			
3-H			0.173 ± 0.001			
7–M	2	0.13–0.53	0.303 ± 0.003	114.0 (2.6) 9.1 (0.2)	151.0 (3.9) 8.9 (0.3)	147.7 (2.2) 10.9 (0.3)

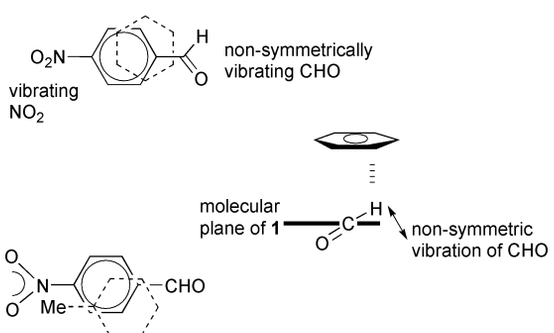

Fig. 2 Complexes of **1** with **B** and **T**. Schematic drawings of complex centre (top) and average topology (right, view from the CHO side).

practically equal in the three **B** complexes but *IK* values for the *meta* protons show that the substituent R (R ≠ H) of the vibrating RC=O pushes the complexing **B** closer to the nitro group and that this effect is stronger with the chloro atom. The latter can be expected when this pushing includes dipole–quadrupole interactions that are attractive with the methyl of **2**. This simple logic will even lead to different complex topologies for **2–B** and **3–B** since the dipole character of RC=O in **1** and **2** will change the vibrational behaviour in the complex by repulsive (to O) and attractive (to R) dipole–quadrupole interactions. With a positive partial charge of R the RC=O vibrations are not symmetric in the complex: on average H or Me are nearer to the complexing **B** than the oxygen. A schematic presentation of this complex topology with non-symmetric vibration of CHO is given in Fig. 2, right. For CHO of **1–B** this means an increase of *IK* resulting both from the shorter distance to the shielding **B** and from lessened deshielding by the intramolecular ring current effect. Then the above equidistant complex centre has to be corrected by pushing **B** nearer to the *ortho* protons (Fig. 2, top). This increases the contact interface when one considers the van der Waals dimensions of **B** not shown in Fig. 2. Strong evidence for the deduced non-symmetric vibrations of CHO in **1–B** is given below.

Signals of **2** in CCl_4 at −15 °C are shifted downfield relative to 25 °C by 0.0424 (Me), 0.0330 (*ortho*) and 0.0313 (*meta*) in accord with torsional vibrations. At −15 °C R is much more deshielded in **2** (R = Me) than in **1** (R = H) in accordance with the bond length in the vibrating RC=O. Then, identical *IK* values of R in **2–B** and in **1–B** may point to a steric hindrance of the non-symmetric vibration of MeC=O as a result of bond length and steric demands. In **3–B** the ClCO vibrations will be symmetric since R has no positive charge. *IK* values of **3–B** place the complex centre closer to NO_2 than to COCl in accord with the steric demands of Cl. Signals of **3** in CD_2Cl_2 (internal TMS) at −80 °C are deshielded by 0.096 (*ortho*) and 0.105 (*meta*) relative to +25 °C.

Complexing of 1 with toluene

Complex **1–T** provided (Table 1) a smaller *K* and much greater (by 29–40%) *IK* values than **1–B** in spite of very similar *IK* ratios for both complexes (CHO : *ortho* ≈ 1 and *ortho* : *meta* = 1.2–1.3) that indicate very similar topologies. The large difference in magnitude of *IK* contrasts with the results reported for the **T** complex of 1-ethyltheobromine **ET** (Fig. 1) whose *K* increased relative to **ET–B** while *IK* values did not change much and decreased rather than increased.[2] A decrease in *K* for **1–T** may result from a vibrating nitro group whose repulsive action is increased by the methyl group of in-plane rotating **T**. This is illustrated by a comparison of the molecular dimensions in Fig. 2, bottom, when van der Waals dimensions of the methyl group are taken into account. In-plane rotation of D can always be expected unless there is an extra fixation of D.

The higher ring current effect (in the wider sense)[13] of **T** as compared to **B** resulting from the electron donating methyl group can give at most a 13% increase of *IK* for **1–T**. The abnormal uniform increase or at least the major part of it can only come from a ternary complex with two **T** both covering the same part of **1** yielding a face-to-face complex of type ADD. Type DAD can be excluded since it should arise from **T** and **B** in comparable amounts with only small differences in *IK* values. The only relevant property discriminating **B** and **T** is the latter's dipole moment (0.36 debye).[18] Type ADD may therefore be considered to arise by complexing of **1** with the stacking dimer $\mathbf{T}_2$ of **T** (Fig. 3, top). $\mathbf{T}_2$ has the **T** dipoles antiparallel preventing

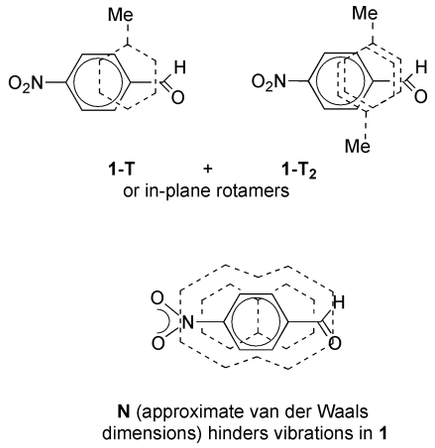

Fig. 3 Complexation of **1** with **T** and **N**, schematic presentation.

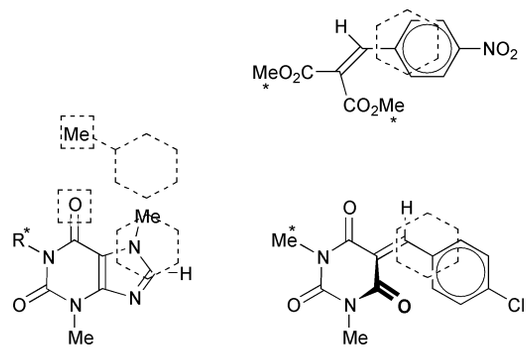

Fig. 4 Main complex centres (approximate) of **C**, **ET**, **4** and **5** indicated by benzene hexagons (on rear face of **5**), minor centres indicated by asterisk. Molecular dimensions for the main complex of **C** or **ET** with **T** illustrate dipole–dipole attraction when the methyl of **T** covers the oxygen in position 6.

an attractive dipole interaction with a third component. Stacking is the preferred dimerization of **T** according to recent calculations.[18] From the temperature dependence of chemical shifts (CCl_4, TMS) the self-association of **T** had previously been deduced to be more extensive than its association with two non-aromatic solutes (non-aromatic A).[19]

The idea that **1** and $\mathbf{T}_2$ form a complex gives rise to two questions. First, why does **ET** not show any sign of a complex with $\mathbf{T}_2$? Second, how can the results in Table 1 indicate a pure 1 : 1 complexation by congruence in *K*? **C** and hence also **ET** have a dipole moment (**C**: 3.70 debye)[20] and a peripheral complex topology (Fig. 4, left). The complex centre lies near positions 7 and 8 (*cf*. Fig. 4, left); cutting away atom groups 7–9 leads to dimethyluracil **DU** (Fig. 1) whose corner-on complexes are mentioned in the Introduction.[2] The (main, see below) complex centre of **C** and **ET** shown in Fig. 4, left, is close to the positive pole of the molecular dipole in accord with the direction of the dipole.[20] Hence, face-to-face attachment of **T** can proceed such that the dipoles of **T** and **ET** attract one another, *viz*. with the ring of **T** over the complex centre and with the methyl group (positive pole of **T**) exactly over the neighbouring oxygen of **ET** as is easily recognized from the molecular dimensions of **ET** and **T** in Fig. 4, left. This dipole–dipole extra stabilization increases *K* from 0.092 (**ET–B**) to 0.107 M^{-1} (**ET–T**) at least in part.[2] Dipole interaction between $\mathbf{T}_2$ and **ET** would yield an association of three dipoles which easily expels one of them so that formation of **ET**–$\mathbf{T}_2$ would be insignificant as compared to **ET–T**. Dipole–dipole attraction between A and **T** is not controlled by the total dipole moment of A, it rather requires a good correspondence of **T** with the distance between the complex centre of A and an atom or atom group of A with high negative partial charge, usually an oxygen atom. Of course, **T** in **ET–T** will not rotate in plane. A dipole moment of 2.35 debye in CCl_4 has been reported for **1**.[21] Comparison of molecular dimensions in Fig. 2, bottom, shows that **T** with its ring covering the complex centre of **1** (Fig. 2, top) cannot place its methyl over one of the oxygen atoms. In contrast, the methyl group would rather be repelled by the nitrogen through its high positive partial charge.

The second question has to deal with equilibria (6)–(9). AUS

$$\mathbf{1} + \mathbf{T} \rightleftharpoons \mathbf{1–T} \quad (6)$$

$$\mathbf{1} + \mathbf{T}_2 \rightleftharpoons \mathbf{1–T}_2 \quad (7)$$

$$\mathbf{T} + \mathbf{T} \rightleftharpoons \mathbf{T}_2 \quad (8)$$

$$\mathbf{1–T} + \mathbf{T} \rightleftharpoons \mathbf{1–T}_2 \quad (9)$$

effects are insignificant because equilibria (6) and (7) have the same a_1 and will differ little in a_2 since only a disproportionately small part of non-specific shielding of A protons can come from the direction where the complexing D is attached.[3] Without dipole–dipole attraction in **1–T** the same forces operate both in **1–B** and **1–T** with a difference in dispersion forces of perhaps 20% that may be compensated by the described steric repulsion between rotating **T** and vibrating NO_2. Calculations on stacking dimers of **B** and **T** have given about a 40% increase of dispersion effects by the extra methyl group in the two **T** molecules corresponding to 20% for one **T**.[18] Aldehyde **1** may attach to $\mathbf{T}_2$ as easily as to **T** with an identical repulsive interaction between Me and NO_2. The thermodynamic stabilities of **1–T** and **1**–$\mathbf{T}_2$ (Fig. 3, top) relative to **1** and **T** or **1** and $\mathbf{T}_2$, respectively, will not significantly differ if at all; dispersion forces are probably equal within free and complexed $\mathbf{T}_2$. Then the system of the four equilibria may be described approximately by (6) and (7) with numerically equal *K*. When only these 1 : 1 complexations are considered the identical *K* from the three proton sites is not surprising. The experimental *K* may be the weighted sum of the constants for equilibria (6) and (7) where the difference in concentrations [**T**] and [$\mathbf{T}_2$] is taken into account. The ratio [$\mathbf{T}_2$] : [**T**] is not constant but depends on [D_0] which ranges from <1 to >8 *M* in both experimental series. K_{1+T} of equilibrium (6) is probably a bit smaller than *K* in Table 1. The results in Table 1 are not in contrast to the proposed complexing of **1** with both **T** and $\mathbf{T}_2$. *K* values may not always indicate a minor 1 : 2 complex with **T** by incongruity. **1**–$\mathbf{T}_2$ provided for the first time a well-founded idea of how a 1 : 2 complex is arranged.

The naphthalene complex of 1; hindrance of torsional vibrations

1–N provided (Table 1) in a very careful study surprising results as compared to **1–B**. The increase in *K* was larger than expected; *IK* values (*ortho* ~ CHO > *meta*) point to similar topologies, but their size did not change in contrast to other studies and despite a doubled (2.17 : 1)[13] ring current effect. Depending on distances between proton and complex centre, *IK* increased by 25–75% for complexes of caffeine (**C**) and by 24–73% for those of 1,3,7,9-tetramethyluric acid (9-methyl-8-oxo-8,9-dihydro-**C**) on going from **B** to **N**.[2,17] The low percentages are derived from high *IK* values. *IK* becomes less and less sensitive to stronger shielding with increasing *IK*; 10^2*IK* finally reaches a maximum at about 230 ppm for face-to-face complexes.[2,17] One exception (fervenulin, MeNCH of **C** replaced by N=CH–N, ring expanded) was reported without discussion at a time when signal independence of *K* was the only problem.[9] There are probably at least two isomeric complexes with the small **B** and a single complex with the large **N**.

The abnormal behaviour of **1–N** is also found with the furan analogue of **1**. This more complicated case will be reported elsewhere but it shows that a special phenomenon accounts for the abnormal *IK* values. The upfield shifts in free **1** as well as in

1–B arising from vibrations may be compensated at least in part by a more planar **1** in **1–N**. This idea of a more planar **1** in **1–N** as the origin of abnormal *IK* values gave the impulse to study the temperature dependence of chemical shifts. The large **N** hinders vibrations of NO_2 and CHO, the latter more so than the former (Fig. 3, bottom). This hindrance increases the contact interface and hence the dispersion forces. The small **B** in **1–B** cannot make use of a (nearly) coplanar CHO in the same manner. Planarization in **1–N** may sufficiently explain the near-constancy of *IK* for the aromatic protons but insufficiently for CHO, as the low temperature shifts in CCl_4 show. The constancy of this *IK* primarily requires the upfield shift to come from the described non-symmetric vibration in **1–B**.

The unusual effects of *IK* (CHO) in **1–B** and **1–N** may be roughly estimated as follows. The ring current model of Johnson and Bovey[22] using intramolecular distances obtained by AM1 provided an upfield shift for an orthogonal CHO in **1** relative to a coplanar CHO of 0.2–0.3 ppm. Shift calculations by Abraham and his co-workers using his model gave the probably more precise value 0.24 ppm.[23,24] At 25–30 °C the vibrations may contribute a substantial part of this 0.24 ppm as the upfield shift for CHO of free **1** relative to planar **1**. This part is close to the downfield shift for the more planar **1** in **1–N** and may amount to 0.1 ppm including resonance effects. The upfield shift for the non-symmetric vibration in **1–B** may also be taken as 0.1 ppm. Shortening the distance to **B** in **1–B** from an assumed 35 nm to 32 nm would bring about a 0.3 ppm upfield shift in **1–B** according to ref. 22 so that without these effects *IK* (CHO) may be 0.5 ppm higher for **1–N** than for **1–B** corresponding to a 27% increase. When the downfield shifts in CCl_4 at −15 °C reflect the planarization effects in **1–N** one obtains from 0.1 ppm for CHO, 0.35 ppm or a 24% increase for *ortho*, and 0.38 ppm or a 35% increase for *meta* protons.

Benzene complexes of 4 and 5

H–C=O of **1–B** is replaced in **4–B** and **5–B** by a much less polar H–C=C so that dipole–quadrupole interactions with **B** are impossible, making *IK* of this proton smaller than in **1–B**. None of the above discussed vibrations are possible in **4** and **5** since coplanarity of *cis*-ArC=CCO is prevented by an *ortho* proton. The most striking finding as against **1–B** is the small *IK* for HC=C in **4–B** and **5–B** (Table 1). Ignoring the methyl groups (see below) and the m_2 values, parameters of **4–B** are in accord with a 1 : 1 complex and with an unchanged topology; they do not differ by more than 7% from those of **1–B** except for *IK* of HC=C and the small *K*. Poor electron withdrawal by $HC{=}C(CO_2Me)_2$ and steric hindrance make *K* small. A more coplanar *cis*-ArC=CCO in complexed **4** (Fig. 4, top) and the flexible ester groups may perhaps also contribute to the smallness of *IK*. The significant deviation of *K* obtained for the methyl groups (Table 1) indicates higher complexes, but the distances between complex centres make treatment as separate 1 : 1 complexes successful with the good complex centre C=CHAr but not with the weak methyl centres (asterisk in Fig. 4, top).

Poorly soluble chloro compound **5** (Fig. 1) was studied because of the insolubility of nitro compound **6** (Fig. 1) that may be regarded as an analogue of **4** with little conformational flexibility of O=C–C–C=O. The signals of **5** in CCl_4 at −15 °C are found downfield by −0.0012 (C=CH), 0.022 (*ortho*), 0.021 (*meta*), −0.0013 and 0.0020 for *N*-Me relative to those at 25 °C. This does not indicate a vibration; the aromatic shifts point to a stacking arene–arene dimerization. **5–B** provided the same *K* from all proton sites showing that the poly complexation with **4** changes to an isomeric complexation of **5** with two or three centres: C=CHAr (highest *IK* for *ortho* and =CH) and one or both *N*-Me groups (Fig. 4, right). Due to the large intramolecular distances a single **B** molecule cannot cover all proton sites of **5** and gives rise to 10^2IK = 61–100 ppm for each proton

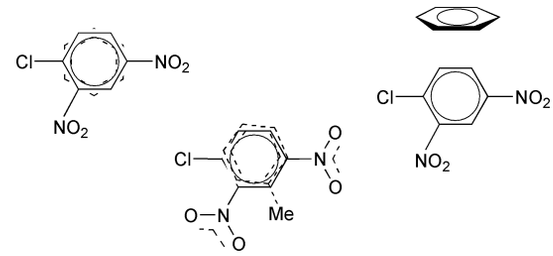

Fig. 5 Approximate topologies for isomeric complexes of **7** with **B** (left) and **T** (centre). Main complex is face-to-face, minor complex is edge-on (right, shown for **7–B** only).

group. The small range indicates that none of the complex centres predominate pronouncedly. Approaching a more planar C=CAr by taking on an optimal skewed conformation of *cis*-CO_2Me is rather easy for **4**. There must be an analogous off-plane pushing of *cis*-CO in **5** (Fig. 4, right) as is already indicated by the sharp IR band at 1731 cm^{-1} besides the strong C=O band at 1668 cm^{-1}. This off-plane C=O provides a simple explanation for the isomeric complexes. The off-plane oxygen prevents any complexation on this face of **5**. Complexation of the rear face is possible but when the centre C=CHAr is occupied in this way by **B** (van der Waals dimensions are not shown in Fig. 4) there is no place for a second **B** over an *N*-methyl and *vice versa.* Signals of central protons (HC=C and *ortho*) are downfield shifted by more than one of these isomeric complexes, as shown by their relatively high *IK*. Both the chemical shift and the higher *IK* of Me1 (Table 1) are compatible with a planar imide structure (asterisk). These arguments for the isomeric complex are strengthened by an isomeric complex given below with **C** that is related to **5** in structure and in relative positions of complex centres (Fig. 4, left).

Complexes of 1-chloro-2,4-dinitrobenzene 7

The behaviour of **7** (Fig. 1) deviates in various respects from that of **1**–**5**. Dipole moments from 3.0 to 3.31 debye have been reported for **7**.[25] Its temperature dependence of chemical shifts supports the idea of the joint or total anisotropy of the whole molecule proposed above for **1**. In CCl_4, signals of **7** at −15 °C are found downfield relative to +25 °C by 0.05 (3-H), 0.04 (5-H) and 0.0330 (6-H); at −15 °C line broadening provided only one line for 3-H and three lines for 5-H. The separately considered anisotropy effects in a more planar **7** would give zero for 6-H (ring current only), a certain shift for 5-H and by far the largest shift for 3-H. Resonance effects can lessen the electronic shielding of 3-H and 5-H but not of 6-H. The total anisotropy (benzene ring + nitro groups) can explain the 6-H shift.

Parameters of the **7** complexes are listed in Table 2. *K* increases from **7–B** to **7–T** in analogy to **ET** but stronger. *IK* values in Table 2 are always in the order 6-H = 5-H > 3-H, indicating similar topologies. The *IK* difference between 3-H and the other protons comes at least in part of an isomeric complex (see below) so that the main complexes will have the benzene ring of **7** covered by the ring of **B**, **T** or **M** rather precisely centre over centre (Fig. 5, left). No **7**–$\mathbf{T}_2$ is indicated by increased *IK* values; in contrast, on going from **B** to **T** each *IK* decreases. Steric repulsion of the methyl group by vibrating nitro groups is not compatible with the increased *K*. With the same topology for **7–B** and **7–T** the methyl group of **T** will be placed over the negative pole of **7**, between the two nitro groups (Fig. 5, centre). The dipole moment of **7** forms an angle of about 20° to the line from 3-H to 6-H.[26] The drawing in Fig. 5 is adapted to this orientation. A slight change of the topology by the interaction of the dipoles may perhaps decrease *IK* for 3-H but not simultaneously for 5-H and 6-H.

K from 3-H is uniformly lower than the average calculated from all signals of **7–T**. The two *K* values calculated separately from 3-H and from the other protons seem to be more accurate

(Table 2). When this deviation in K is significant it points to an isomeric minor complex of the edge-on type with 6-H and 5-H standing on **T** (analogous to Fig. 5, right) and therefore providing a more than proportional contribution to IK of these protons. Such isomeric complexes may be expected from the structure and dipole moment of **7** and can explain the finding that two IK values of **7–B** are greater than the greatest IK value so far obtained from a face-to-face complex with **B**, namely $10^2IK = 186$ ppm.[2] Edge-on complexing will form both edge-on **7–T** and edge-on **7–T$_2$** with the latter's K (**7** + **T$_2$**) in addition to the joint K from both isomeric 1 : 1 complexes. 3-H suffers least if any from this complication since its IK for both edge-on complexes must be small. Then, the real K for total 1 : 1 complexing should be near 0.173 M^{-1} and K for the edge-on association of **7** with **T$_2$** near 0.01 M^{-1}. The ratio $R_{iso} = K_{main}/K_{minor}$ would then be near 15. R_{iso} depends on D when a D-specific extra stabilization of the face-to-face complex increases $K_{face\text{-}to\text{-}face}$ relative to $K_{edge\text{-}on}$. Thus, the dipole stabilization in **7–T** makes R_{iso} greater than with **7–B**. A small R_{iso} of **7–B** and thus a relatively large $K_{edge\text{-}on}$ can make the edge-on contributions to IK for 5-H and 6-H of **7–B** larger than those of the two **T** complexes, despite the extra contribution from edge-on **7–T$_2$**. The 10% decrease of IK for 5-H and 6-H on going from **B** to **T** may be due to this change of R_{iso} that also may influence IK of 3-H. Because this seems to be the only possible explanation for the IK values, the slight proton dependence of K will be significant. Compound **7** standing with 5-H and 6-H on D resembles corner-on complexes of 1,3-dimethyluracil **DU** (Fig. 1) that stand with 6-H on D.[2] Its K for the **B** complex was only 0.079 M^{-1} while 10^2IK for 6-H was 304 ppm. An even smaller $K_{edge\text{-}on}$ for the edge-on complexes of **7** as well as the change from corner-on to edge-on may arise from the repulsive influence of the chlorine atom in accordance with the reported difference between **C** and 8-chlorocaffeine.[2] The main complexes of **7** are undoubtedly the face-to-face complexes. Assuming that for **7–B** $R_{iso} = 5$ and edge-on $10^2IK = 300$ ppm gives 60 ppm as the edge-on contribution to the obtained 10^2IK values for 5-H and 6-H of **7–B**, so that 10^2IK of the face-to-face complex would be about 140 ppm for these protons. This appears reasonable and the order of magnitude is in accord with the above interpretation.

Complexing of **7** with **M** (Table 2) provided reliable results since the signals of **7** were sufficiently downfield of the **M** signals. The rather high K as well as the low IK values point to an effect similar to but weaker than that described for **1–N**. In-plane rotating **M** offers a rather large face for complexing that may hinder vibrations of the nitro groups, giving low IK values by downfield shifts of a more planar **7** relative to free **7**. This effect of hindered vibrations should be largest for 3-H and, indeed, the proportional decrease of IK values on going from **7–B** to **7–M** is greatest for 3-H. The large $K_{face\text{-}to\text{-}face}$ will make $K_{edge\text{-}on}$ negligible, so that the edge-on contributions to IK will probably approach zero. This will also contribute to the smallness of IK values.

The above finding for **7–T** shows again that proton independence of K is not a stringent demand for **T** complexes and it shows that a study with **T** in a series of D may be particularly helpful for the detection of isomeric complexes. This will be the subject of a forthcoming paper, but we will mention one finding from this paper here in support of the complex isomerism of **5–B**. K (0.129 M^{-1}) for **C–T** obtained from 7-methyl and 8-H is greater than K (0.107 M^{-1}) for **ET–T** in accordance with the general behaviour of all investigated **C** and **ET** complexes resulting from steric hindrance by the ethyl group of **ET**.[2,5] But for **C–T** the following results were obtained: $K = 0.065$ M^{-1} from 1-Me and $K = 0.093$ M^{-1} from 3-Me. This contrasts with previous results since **C** complexes with 16 different D compounds always gave a good congruence in K.[5] 1-Me or 1-CH$_2$, respectively, and 3-Me show the greatest changes in IK values on going from **ET–T** to **C–T**: IK increases by the factors 3.6 for the 1-substituent and 1.7 for 3-Me. This clearly indicates a minor complexation over 1-Me of **C** (Fig. 4, left) with a particularly large IK resulting from a **T$_2$** contribution. A dipole–dipole attraction can be excluded since 1-Me is flanked by two oxygens with a distance between 1-Me and oxygen that is too short for a dipole–dipole attraction of **T**. The corresponding IK factors 2.4 and 1.1 for the **B** complexes show again a minor complexation of 1-Me.[2] In the original paper on **C** complexes a discussion of IK values for 1-Me and 3-Me was already considered necessary since they appeared difficult to reconcile with the deduced complex topology.[5] For 7-Me and 8-H in **C–T** the main association dominates so strongly that a disturbance by the minor association is insignificant. For 1-Me and 3-Me the difference between K_{minor} and K_{main} is the same, but the effective Δ_0 contributions may become comparable in magnitude. Then one cannot expect consistent results from these Δ_0 values when they are regarded as resulting from pure 1 : 1 complexation. The 1-Me contributions from the minor complexes with **T** and **T$_2$** may perhaps be even larger than the small contributions from the main complex.

Résumé of the toluene complexes

Three variants of complexing with **T** have been described or mentioned above. **ET** forms only a single 1 : 1 complex since the isomeric complex suffers from steric hindrance. Compound **1** complexes both with **T** and **T$_2$** at the same centre, again without disturbance by isomeric complexes. Compounds **7** and **C** form isomeric complexes with **T** and they form **T$_2$** complexes only with the weaker centre, but complexes with **7** and **C** differ in R_{iso}. With **7** this is near 15 and so computation of K is not seriously influenced. With **C**, R_{iso} is <5 (3.8 calculated from K values of **C–B** and **ET–B**)[2] so that computation of K is seriously disturbed when Δ_0 contributions from main and minor centres are comparable in size, as for 1-Me and 3-Me.

Temperature dependence of CH signals

Temperature dependence (Table 3) of chemical shifts (ppm downfield *vs.* internal TMS) may have at least three origins: interactions with a polar solvent, solute–solute interactions and conformational changes including torsional vibrations. In CCl_4 the shifts come mainly from restricted vibrations, except for **C** (see below). Polar solvent–solvent self interactions for CD_2Cl_2 (0.0105) and CD_3COCD_3 (0.074) are detected from downfield shifts for the residual protons. The largest shift in Table 3 is from 8-H in **C**, pointing to a strong dipole–dipole interaction with O=C of the solvent CD_3COCD_3; the positive pole of **C** (3.7 debye) is near 8-C. The shifts of **C** in CCl_4 can only arise from dipole–dipole self interaction of the poorly soluble **C**. Shift comparisons for **1** (2.35 debye) are compatible with torsional vibrations as the main origin in the three solvents. Polar effects are more important with **7** (3.0–3.31 debye) in polar solvents; they can be large with highly polar solutes (*e.g.* benzonitrile, 0.22 for *ortho*).

Experimental

Procedures, instruments, external references, further details and computations were described previously.[2,4,8,13,17] The accuracy of Δ_0 was ≤0.0016 ppm. The temperature for complex formation was 30.0 ± 0.3 °C. [A$_0$] was 0.0089–0.0210 M but about 0.075 M for **7–M**. The preparation of n (12–18) solutions was conducted with the utmost accuracy from two stock solutions of known density at 20 ± 0.5 °C by means of a microsyringe under mass control and avoidance of volatilization losses. The same capillary for the external reference (dioxane with **M**) was used throughout the series. Chemicals were used as purchased. Compound **5** was prepared from 4-chlorobenzaldehyde and 1,3-dimethylbarbituric acid analogously to **6**:[27] mp 163 °C (Found: C, 55.8; H, 4.1; N, 9.9%, $C_{13}H_{11}ClN_2O_3$ requires C,

Table 3 Downfield shifts in ppm of **1**, **7** and **C** on cooling in various solvents

	$\Delta\delta$		
	CCl_4 +25 °C ⟶ −15 °C	CD_2Cl_2 +25 °C ⟶ −80 °C	CD_3COCD_3 +25 °C ⟶ −80 °C
1 CHO	0.0115	0.063	0.058
1 *ortho*	0.040	0.105	0.112
1 *meta*	0.044	0.097	0.102
7 3-H	0.05	0.155	0.180
7 5-H	0.04	0.128	0.189
7 6-H	0.033	0.119	0.146
C 1-Me	0.0027		0.0040
C 3-Me	0.011		0.0075
C 7-Me	0.022		0.023
C 8-H	0.037		0.278

56.0; H, 4.0; N, 10.0%); ν_{max}/cm^{-1} (KBr) 1731 (C=O), 1668 br (C=O); δ ($CDCl_3$) 3.39 (s, Me), 3.41 (s, Me), 7.43 (d, *J* 8.6, *m*-H), 8.03 (d, *J* 8.6, *o*-H), 8.49 (s, C=CH). The precision of the temperature dependence of shifts (Bruker Avance 300 instrument) was limited by changes of the respective multiplet.

Chemical shifts Δ_0 were measured in Hz and used as such in all calculations. Hz was converted to ppm in the final results. Each Δ_0 was the mean of three measurements unless the first two coincided. Δ_0 of doublets was usually taken from the stronger line unless the weaker line had a much lower least square sum (SDDQ in the programs). A doublet of doublets was analogously treated to give two Δ_0, usually from the two main lines. With **7** all lines were taken and the means taken from these. *K* is the mean of all lines measured; *IK* and m_2 are means of the separately found values.

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