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Weak Arene Complexes of Nitroaromatics. ^{1}H NMR Studies of Conformations and Polar Effects. *syn-anti* Selectivity of 5-Nitrofurfural

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Arene Complexes in CCl_4, Formation Constants, Topologies

The refined ^{1}H NMR method (AUS concept, CCl_4) provided association constants *K* and approximate complex shifts *IK* for complexes of nitroaromatics A with aromatic hydrocarbons D. 5-Nitrofurfural (**1**) and benzene (**B**) or toluene (**T**) form ***syn*-1B** or ***syn*-1T**, respectively; a proton dependence of *K* indicates about 10% *anti* complexes. The dimer $\mathbf{T}_2$ of **T** additionally yields some $\mathbf{1T_2}$ since *IK* values are 29–34% higher than for **1B**. With naphthalene (**N**) or phenanthrene all protons of **1** provide the same *K*. Picrylacetone (**2**) and **B** form **2B** and at least one **2BB** adduct; published parameters of **2B** and **2BB** are inconsistent. **2** and **N** or **M** (1,3,5-trimethylbenzene) form only 1:1 complexes. All results are in accord with CH_2COMe standing perpendicular to picryl. 2,4-Dinitrophenylacetone (**3**) in a rather flat conformation coordinates with a single stacking **N** centred over C-6; **3** yields two isomeric stacking complexes **3B** and at least one edge-on **3B** complex. 2-Chloro-5-nitropyridine (**5**) forms stacking complexes under repulsion of D by the ring N. In contrast to **1** and 4-nitrobenzaldehyde (**6**) 1,4-dinitrobenzene (**7**) and **T** form only a 1:1 complex that is stabilized by dipole-dipole attraction. Equal and unequal shielding of proton pairs (ortho or meta) in complexes of type **6B** is discussed.

Introduction

Formation of complexes AD from compounds A and aromatic hydrocarbons D was often studied with NMR methods, in particular when A was a nitroaromatic compound [1–4]. The efforts concentrated on the determination of formation constants *K* but for weak complexes often with unsatisfactory results [2]. Consistent results for weak complexes and full exploitation of the potential inherent in ^{1}H NMR can be reached when solvent effects are excluded as far as possible and when non-specific NMR effects resulting from the necessary excess of D are quantitatively considered both for A (see below) and for an internal reference [5, 4]. Disturbing solvent influences are avoided with the solvent CCl_4 and non-linear effects on the reference signal are avoided by an external reference. Only one possible internal reference is known [6,7] whose *cis*-methyl signal position depends linearly on concentrations of D, *viz*. 1-chloroisobutene (1-chloro-2-methylpropene) CLIB.

When the above requirements are taken into account (AUS concept) [5, 4], separate data reduction for each group of isochronic A protons provides *K* and an approximate complex shift *IK* arising from the complexing D by diamagnetic shielding of this proton group. *K* of weak complexes depends mainly on polar effects, dispersion forces and steric effects [1, 8]. With signals coming of different molecular sites of A their *IK* values usually contain informations about the mean topology of AD, primarily about the complex centre (mean point of A covered by the centre of D) in stacking complexes [1, 8]. Further influences on *K* and *IK* come of dipole-dipole and dipole-quadrupole interactions, impediment of torsional vibrations, formation of edge-on and of isomeric complexes [1]. Torsional vibrations in aromatic compound A make signals go a little upfield by decreasing the effects of resonance and magnetic anisotropies [1]. Distinct influ-

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ences of conformations or of conformational flexibility in A were not observed so far. Some findings may be useful for studies of host-guest complexes.

Method

A concise description of the AUS method was recently given [1]. This modification of the well-known Scatchard-Foster-Fyfe (ScFF) method arose from interrelated findings [6] with varying concentrations of benzene **B** (C_6D_6) in CCl_4: (a) a non-linear ScFF plot turning from the negative to a positive slope for the least shifted signal of caffeine when internal TMS was the reference and (b) a quadratic term in the dependence of the TMS signal relative to an external signal. The very large concentration range possible with **B** (up to > 10 M) made such effects easily detectable. The small range with D = hexamethylbenzene was probably the main reason why the influence of internal TMS was overlooked in a previous comparison [9] of internal and external referencing. The reported shifts (INT) with internal referencing were always smaller and even after susceptibility corrections of the externally referenced shifts (EXT) there was a clear trend that was the more distinct the higher the concentration of this D was despite the small upper limit of 0.22836 mol/kg solution. INT was smaller than EXT by 0.1–1.2 Hz in 27 probes, equal to EXT in 4 probes and greater than EXT by 0.1 Hz in 3 probes.

The AUS concept takes into account non-specific shielding of A protons by D (total concentration $[D_0]$) using linear shift corrections a_1 $[D_0]$ for A and a_2 $[D_0]$ for AD. The change of magnetic susceptibility with $[D_0]$ is considered [4] by b $[D_0]$. Then, equations (1)-(5) replace the ScFF relation $\Delta_0/[D_0] = -K\Delta_0 + K\Delta_{AD}$. Definition of Δ_0 and Δ_{AD} follows; *Icpt* replaces the intercept $K\Delta_{AD}$. Total A concentration $[A_0]$ is made small while $[D_0]$ in an experimental series of n solutions is evenly distributed over the largest possible range. A small $[A_0]$ is advantageous for the methodical requirement $[D_0] >> [A_0]$ but it also makes chemical shifts less sensitive to possible self associations of A (*cf.* Table 3 in [1]) that may influence Δ_0 for low $[D_0]$. Δ_0 is the difference between chemical shifts of A in absence of D and in presence of $[D_0]$. *IK* is an approximation for $\Delta_{AD} = (\delta_A\ \delta_{AD})$ of the classical model or, more precise [5,4], $\Delta_{AD,00}$ of the AUS model. *IK* and m_2 are obtained for each signal of A; m_1 remains unknown but resembles m_2 in size. *IK* depends on the diamagnetic anisotropy of D and on distances in AD enabling conclusions on the mean topology of AD. For further details and computer programs Sc-AUS, based on the ScFF method [10] and CA-AUS, based on the Cresswell-Allred method [11] see [1, 4, 9]. Sc-AUS is usually more sensitive to experimental scatter [12].

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

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

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

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

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

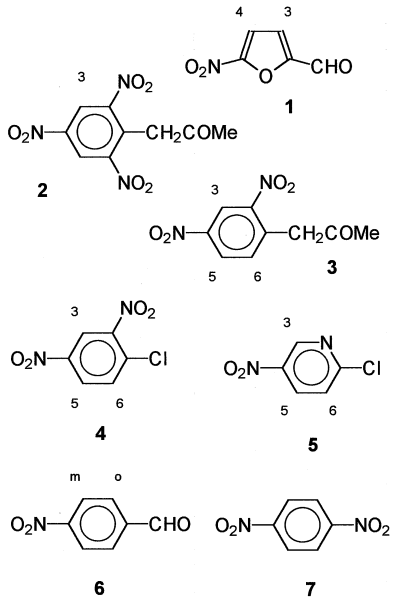

Fig. 1. Structures of compounds A; numbering and labels of proton sites.

Results and Discussion

Results obtained with **1** (Fig. 1) are presented in Table 1, results with **2**, **3**, **5** and **7** in Table 2. **B** stands for deuterated benzene (C_6D_6), **T** for deuterated toluene (C_7D_8), **M** for mesitylene (1,3,5-trimethylbenzene), **N** for deuterated naphthalene ($C_{10}D_8$) and **P** for phenanthrene. SF is the saturation fraction $[AD]/[A_0]$. Only CA-AUS results are reported, the Sc-AUS results did not significantly deviate. m_2 values are reported but usually not discussed. Any temperature dependence of chemical shifts for CH signals is given in the discussion.

Table 1. Parameters of complexation of **1** from *m* experimental series; rounded parameters of complexation of **6**[a].

AD	*m*	SF	K / M^{-1} (max. dev.)	10^2 *IK* (max. deviation) / ppm 10^2 m_2 (max. deviation) / ppm M^{-1}		
				CHO	3-H or *ortho*	4-H or *meta*
1-B total	1	0.11–0.62	0.149 (0.009)	140.6 5.9	147.4 (5.4) 8.0 (0.2)	144.8 (1.7) 7.4 (0.1)
CHO 3-H + 4-H		0.140 0.154 (0.003)				
1-T total	2	0.10–0.54	0.138 ± 0.007	189.8 (1.0) 6.0 (0.2)	190.4 (0.6) 8.1 (0.1)	186.9 (0.7) 7.7 (0)
CHO 3-H + 4-H		0.130 (0.009) 0.143 ± 0.001				
1-N	2	0.08–0.50	0.508 ± 0.011	108.5 (2.6) 20.1 (0.4)	152.7 (3.6) 26.2 (0.6)	144.7 (4.0) 22.9 (0.5)
1-P	3	0.11–0.44	0.814 ± 0.004	148.8 (2.2) 25.1 (1.4)	189.7 (1.4) 36.3 (1.3)	186.2 (5.8) 27.9 (2.3)
6-B			0.125	152	158	123
6-T			0.107	207	204	172
6-N			0.415	143	161	129

[a] Taken from [1].

Complexes of 5-nitrofurfural (1)

Compound **1** is the furan analogue of 4-nitrobenzaldehyde (**6**) (Fig. 1) whose complexes were described recently [1]. The parameters (Table 1) of **1B** and **1T** show K from CHO to be 10% smaller than K from ring protons. A similar result with 1-chloro-2,4-dinitrobenzene (**4**) (Fig. 1) and **T** was found to come of isomeric complexes, *viz*. a stacking complex and a (minor) corner-on complex detectable by enlarged *IK* values [1] arising from corner-on complexes with **T** and its dimer $\mathbf{T_2}$. The 10% K difference for **1B** and **1T** result in another way from isomeric complexes.

Complexes of **1** should resemble those of **6** despite slightly different molecular geometries of 5- and 6-membered rings. In particular one may expect **1B** to have two characteristics of **6B** (Fig. 2: B), *viz*. [1] repulsion of **B** by the torsionally vibrating NO_2 and dipole-quadrupole interaction of **B** with H of the non-symmetrically vibrating CHO. But **1** can form isomeric complexes from its *syn-anti* rotamers (Fig. 2: A). A topology as shown in Fig. 2 (C) would suffer from repulsion of **B** both by the ring O and, less so, by NO_2 which is closer to **B** than in **6B**. Thus, **1** can only yield the complex

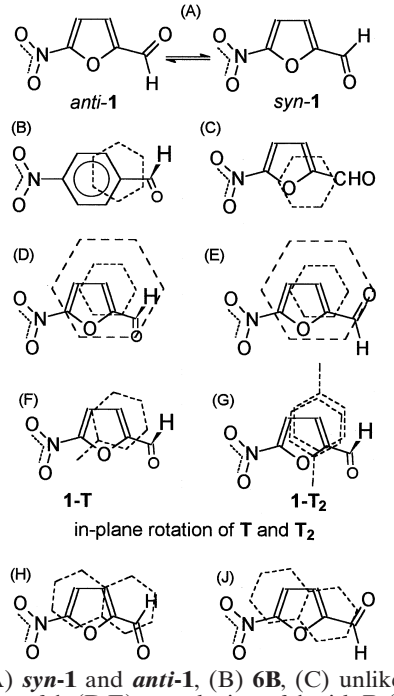

Fig. 2. (A) ***syn*-1** and ***anti*-1**, (B) **6B**, (C) unlikely complex centre of **1**, (D,E) complexing of **1** with **B** (approximate van der Waals dimensions), (F,G) **1T** and $\mathbf{1T_2}$ (both shown for ***syn*-1** only), (H,J) **1N** (*syn* and *anti*).

topologies shown in Fig. 2 (D, E). The position of **B** required for a dipole-quadrupole interaction with H of CHO can only be reached with ***syn*-1B** (Fig. 2: D) making it the main complex. The corresponding topology (Fig. 2: E) of ***anti*-1B** is even destabilized by polar interaction of **B** with O of CHO. Diamagnetic shielding of the CHO proton by **B** is much smaller in this ***anti*-1B** than in ***syn*-1B**. Hence the small amounts of ***anti*-1B** will provide disproportionately small contributions to experimental Δ_0 values for CHO so that its K is caused nearly exclusively by the *syn* complex. There will be no substantial *syn-anti* difference (Fig. 2: D, E) in IK of the ring protons so that their K may be regarded as the sum of both K values. The same line of reasoning holds for the K difference obtained from **1** and **T**. No separate K values for the isomeric complexes can be obtained since each experimental signal is the weighted average of all dissolved species.

Apart from the *syn-anti* isomerism there is indeed a good analogy between complexes of **1** and of **6**. So, the IK values of **1T** are 29–34% higher than those of **1B** indicating complexing both with **T** and $\mathbf{T_2}$ (Fig. 2: F, G) as reported [1] for **6**; the molecular dimensions (Fig. 2: F) exclude a dipole-dipole attraction between **T** and **1** that would make formation of $\mathbf{1T_2}$ negligible. Further, K of the **T** complexes is smaller than K of the **B** complexes since repulsion of D by the vibrating NO_2 is increased by the in-plane rotation of **T** (and $\mathbf{T_2}$). Some differences between **1** and **6** remain. The higher K values for the complexes of **1** may arise both from less repulsion by the vibrating NO_2 owing to the molecular geometry and from stronger polar effects as shown by the higher partial charge (AM1) for the mainly covered HCCH moieties. Despite a likely upfield shift on going from ***anti*-1** to ***syn*-1** (*cf.* furfural below) 10^2 IK for CHO of **1B** or **1T** is smaller (Table 1) than that one of **6B** or **6T**, respectively. This is in accord with small amounts of *anti* complexes and with a less covered CHO proton in *syn* complexes due to different molecular geometries. For IK values of ring protons see below. The temperature dependence for chemical shifts [1] of **1** confirms the mentioned torsional vibrations. Cooling a solution of **1** (0.016 M) in CCl_4 from 25 °C to −10 °C made the signals go downfield by 0.0165 ppm (CHO), 0.0501 ppm (3-H) and 0.0526 ppm (4-H) as compared [1] to 0.0115, 0.040 (*ortho*) and 0.044 (meta) ppm for **6**.

No NMR data relevant to the *syn-anti* equilibrium constant are known for **1** in contrast to the parent furfural [13–15]. Dipole moments (in debye) of **1** are 2.60 (*anti*) and 6.07 (*syn*) from AM1 calculation, those of furfural [14] are 3.23 and 3.93 (microwave) or 2.67 and 3.67 (CNDO calculation). Ignoring any solvent interaction, AM1 predicts ***anti*-1** to be more stable by 5.5 kJ/mol while for furfural the *syn* isomer was more stable in dimethylether by 4.4 kJ/mol as calculated from the temperature dependence of coupling constants (4-H/CHO and 5-H/CHO) and hence of the *syn-anti* equilibrium [13]. Abraham and Siverns [14] have shown in a thorough review that the coupling 4-H/CHO in furfural (see below) decreases inversely with the polarity of the solvent in accord with the dipole moments. The analogous polarity influence on the *syn-anti* equilibrium of **1** can be neglected in the data reduction since *e.g.* for **1B** the permittivities of CCl_4 and **B** are 2.2 and 2.3. The *syn-anti* assignment of Dahlqvist and Forsén [13] for furfural has to be inverted [15, 14]. Then three final results [13] for furfural (dimethylether, −115 °C) are useful for a discussion of complexes of **1**. The spin coupling CHO/4-H is 0.85 Hz in the *anti* isomer but < 0.2 Hz in the *syn* isomer and the 3-H (CHO) signal of the *syn* isomer is 0.15 ppm downfield (0.18 ppm upfield) of the *anti* isomer. We now found for **1** in CCl_4 at 30 °C a 4-H/CHO coupling of 0.69 Hz indicating a predominance of ***anti*-1** under the assumption that it has about the same coupling constant (0.85 Hz) as *anti*-furfural. This equilibrium coupling decreases to 0.40 Hz when 20% of CCl_4 is replaced by the polar $CDCl_3$. It decreases also on addition of **B**: to 0.62 Hz with $[D_0]$ = 4.8 M and to 0.55 Hz with $[D_0]$ = 9.0 M strongly supporting a preferred complexing of ***syn*-1**.

K (Table 1) for **1N** or **1P** is independent of the proton studied; separate calculation for CHO and the ring protons provided K = 0.510 and 0.507 M^{-1} for **1N** and K = 0.815 or 0.814 M^{-1} for **1P**. This may come of either the absence of *anti* complexes or a decreased *syn* preference. The large arenes D may cover H of CHO so much better than **B** or **T** that the *syn* complexes, *e.g.* ***syn*-1N** (Fig. 2: H) are strong enough to prevent a detectable influence of *anti* complexes. Alternatively the polar interaction

Table 2. Parameters of complexation of **2**, **3**, **5** and **7** from *m* experimental series; rounded complex parameters[a] of **4B**.

A–D	*m*	SF	K / M^{-1} (max. dev.)	10^2 *IK* (max. deviation) / ppm 10^2 m_2 (max. deviation) / ppm M^{-1}				
				Me	CH_2	3-H	5-H[b]	6-H
2-B	2	0.18–0.63	0.165	96.6 (2.0) 7.1 (0.03)				
		0.21–0.68	0.198		132.2 (1.6) 5.6 (0.09)			
		0.25–0.73	0.247			153.6 (0.5) 5.1 (0.04)		
2-M	2	0.12–0.48	0.489 ± 0.012		61.3 (1.3) 10.4 (0.5)	105.7 (0.8) 10.6 (0.02)		
2-N	2	0.15–0.55	1.206 ± 0.036	41.6 (0.7) 17.6 (0.6)	97.9 (2.3) 14.6 (0.4)	153.3 (1.3) 11.9 (0.17)		
3-B	2	0.19–0.51	0.107 (0.002)	113.2 (2.1) 6.0 (0.1)				
		0.19–0.59	0.134 ± 0.004		162.3 (6.4) 5.8 (0.27)	119.9 (1.9) 5.0 (0.08)	145.4 (6.1) 6.9 (0.22)	184.2 (3.6) 6.7 (0.15)
4-B			0.141			172	199	201
3-N	1	0.09–0.41	0.535 ± 0.020	63.8 14.6	149.1 14.1	98.0 (0.1) 9.9 (0.01)	153.6 (1.6) 12.4 (0.22)	200.9 (1.1) 15.8 (0.17)
5-M	1	0.09–0.44	0.235 ± 0.002			96.7 (0.2) 10.0 (0.1)	174.6 (2.2) 8.1 (0.2)	159.6 (1.9) 8.9 (0.1)
5-N	3	0.14–0.46	0.420 ± 0.003			93.6 (1.0) 12.2 (0.1)	201.4 (1.9) 15.7 (0.4)	192.0 (1.0) 18.3 (0.6)
7-T	2	0.12–0.57	0.144 (0.06)					190.0 (2.0) 6.4 (0.1)

[a] Taken from [1]. [b] One of the four lines could not be used with **3N**.

between a large D and CHO in the *syn* complex is rather offset by an increased contact interface in the *anti* complex (see ***anti*-1N** in Fig. 2: J) arising from the size of D and from hindered CHO vibrations. The low *IK* values of CHO are better compatible with the second possibility. Of course, one can expect rather low *IK* values owing to hindered vibrations but the two *IK* values for CHO are too small to arise exclusively in this way as shown by comparison with the ring *IK* values and as corroborated by *IK* comparison of **1N** with **6N** (Table 1). Moreover, the phenomenon of nearly equal *IK* values for **6B** and **6N** is also found with **1N** and **1B** except for the CHO *IK* of **1N** that is too low. *IK* values have the same order in **1P** as in **1N** and are greater in **1P** by 24–37% in congruence with the 30% difference for the above-plane ring current effects of both D [7].

Complexes of (trinitrophenyl)- and (dinitrophenyl)acetone (2 and 3); *complexes of 2-chloro-5-nitropyridine* (5)

Complexing of picrylacetone (**2**) (Fig. 1) with **B** provided (Table 2) significantly differing *K* values for the three proton sites. This is incompatible with the pure 1:1 model. In addition to **2B** at least one complex **2BB** is formed whose **B** molecules are attached to different sites of **2**. Both sites may form isomeric 1:1 complexes of differing strength without an influence on *K*. Possible complex topologies including those for **2BB** are discussed in order to clarify why **2** and **N** do not yield **2NN** (see below).

Already a previous report [3] came to the conclusion that **2** forms complexes **2D** and **2DD** when **D** is benzene or a larger arene D; complex topologies and conformations of **2** were not discussed. Our parameters for **2** and **B** do not agree with

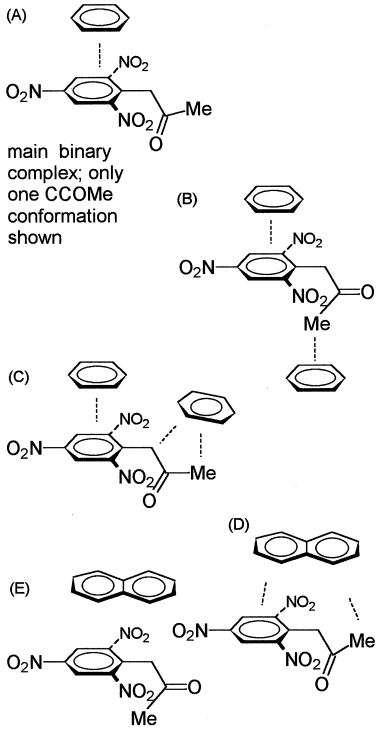

Fig. 3. Possible topologies for complexes of **2**.

those of this study, even with those calculated with the program Sc-AUS. The discrepancy is caused by at least three experimental details of the previous work. First, it is the internal reference (TMS) employed in contradiction to [6] and to the AUS concept as developed in [5]. Sc-AUS must not be used with internal TMS (see section Method). Second, it is the unusual concentration scale, *i.e.* mol/kg solution. There are good arguments [12] that in such studies molarity is the scale of choice. The unit "mol/kg solution" approximates molarity at very high concentrations if they can be reached. On the other hand K from mol/kg solution approximates K_{molal} for dilute solutions [16]. With weak complexes [D_0] has to cover the largest possible concentration range and then there is no linear relation between the scales; densities of D (< 1 g/ml) and solvent (1.59 g/ml) differ too much. For C_6H_6 in CCl_4 1 M corresponds to 0.65, 2 M to 1.36 and 10 M to 10.43 mol/kg solution. Third, it is the use of C_6H_6 that limited the concentration range of D to 0.3–1.5 mol/kg solution equal to 0.47–2.18 M as compared to 1.4–11 M for **2B** in Table 2. Nevertheless, apart from a_2 values ($a_2 = m_2 - b$, eq. (4)) some results show surprising similarities. As compared to the previously from Sc-AUS obtained K values the doubled K values of Table 2 are numerically equal (CH_2), greater by 6% (Me) and smaller by 9% (3-H). IK values are given as Δ_0 in the previous report; they are smaller but have the same order 3-H > CH_2 > Me as those of Table 2, *viz.* (given as 10^2 IK) 109, 108 and 89 ppm. However, the results of Table 2 show much more distinctly that the main centre for 1:1 and 1:2 complexes of **2** lies in the picryl moiety. One would expect that **2B** or most of its isomers have **B** stacking over picryl (Fig. 3: A), possibly shifted towards CH_2 whose positive partial charge is increased by COMe.

Attempts to obtain reliable separate K values (K_1 and K_2) for steps **2** + **D** and **2D** + **D** are doomed to failure since non-specific shielding by D must not be ignored. The previous attempt gave inconsistent results since protons of **2** were more (factor 1.3–2.4 for **D** = C_6H_6) shielded by the second D than by the first D, *i.e.* each complex shift of **2DD** was more than twice that one of **2D** [3].

Intramolecular motions of previously studied compounds A at ordinary temperatures were rotations of methyl groups and torsional vibrations of other groups [1]. In this respect, **2** is a new type of A but its CH_2COMe cannot be flexible since steric requirements (confirmed by space-filling models) and polar effects make it stand perpendicular to the plane of the picryl moiety. Then the main binary complexes may be exemplified by Fig. 3 (A). The oxygen-oxygen repulsion between CO and NO_2 favours the two conformations used for **2-BB** in Fig. 3 (B, C). They enable to attach one **B** to the sterically non-shielded face of picryl and to attach a second **B** over Me as shown in Fig. 3 (B, C) where the two **B** molecules of each ternary complex are sufficiently apart from one another even when van-der-Waals dimensions are considered. The second **B** in Fig. 3 (C) is drawn such as to form a T-shaped complex with CH_2COMe that will be stronger (*cf.* below the T-shaped **2B**) than the alternative complex with the second **B**. Thus, the association of **2** with **B** is likely to form only one ternary complex and two or three binary complexes, *i.e.* the picryl complex with one or two conformations of CH_2COMe plus a T-shaped complex over CH_2COMe arising from polar interactions

(CO dipole, CH_2, Me). Apart from the latter complex the diamagnetic shielding of the picryl protons by **B** must always be strong probably making *IK* of 3-H a fair approximation for all other complexes. *K* provided by 3-H ($0.24\ M^{-1}$) might then possibly come close to K_1 that counts the first step (**2** + **B**).

2N (Table 2) provided the same large *K* from all proton sites showing the absence of a ternary complex. In the previous study of the naphthalene ($C_{10}H_8$) complex the pure 1:1 model was rejected despite finding *K* independent of the proton site [3]. The reported Sc-AUS parameters including a_2 values differed from our parameters due to the same kind of reasons as described above. *IK* values were smaller by 21–34% than those of Table 2; the doubled *K* of Table 2 numerically matches the previous result ($2.3–2.4\ kg/mol^{-1}$). The concentrations of D were in the range 0.03–0.30 mol/kg solution equal to 0.048–0.466 M as compared to 0.15–1.02 M for **2N** in Table 2. The 1:1 model was rejected because a_2 values did not have the expected [5] order Me > CH_2 > ArH. The wrong sequence is caused by non-specific shielding of internal TMS that makes the experimental Δ_0 unqualified for AUS corrections. Our m_2 values have the expected sequence; a_2 and m_2 differ only by the constant *b* (eq. 4). Pure 1:1 complexing with **N** in contrast to multi-complexing with **B** appears reasonable since van-der-Waals dimensions of **N** prevent the formation of a 1:2 complex of the type shown in Fig. 3 (C). Considering these dimensions and the dominance of stacking over picryl suggests that only two isomeric stacking complexes (Fig. 3: D, E) may be formed. A T-shaped complex over CH_2COMe can scarcely compete with stacking whose contact interface with **N** is large making the stability contribution by dispersion forces great apart from a possible charge transfer contribution for stacking **2N**. *IK* values are also compatible with pure stacking, even *IK* of Me. **N** hinders the torsional vibrations of nitro groups thereby increasing the total magnetic anisotropy of picryl (*cf.* [1]). The conformation of **2** shown in Fig. 3 (E) puts Me into the shielding region of picryl. Stacking of **N** over the opposite face of picryl will increase the intramolecular shielding of Me in two ways. First, **N** + picryl shields more than **N** alone analogously to the strong shielding by $\mathbf{T_2}$ in its complexes (*cf.* also the discussion of **3B**, below). Second, impeded vibrations increase the anisotropy of the picryl moiety. The resulting small *IK* for Me is indistinguishable from a direct shielding by **N**. Shielding of CH_2 by **N** is counteracted by hindered vibrations of the neighbouring nitro groups making this *IK* rather small. Of course also *IK* for 3-H will include a counteraction of hindered vibration. This must be expected and is also supported by comparison with **2B** since *IK* values for 3-H are identic in analogy (Table 1) to the *IK* values of **6B** and **6N.** This supports the above interpretations of the 3-H parameters of **2B**.

For **2M** (Table 2) the Me signal of **2** was hidden under **M**. The other two signals were undisturbed and provided results that are compatible with the pure 1:1 model and with topologies analogous to Fig. 3 (D, E). *K* places **2M** between **2N** and binary **2B** as expected. *IK* comparison of **2M** with **2N** shows the weaker diamagnetic shielding by **M**, comparison with 3-H *IK* of **2B** indicates hindrance of torsional vibrations that comes of in-plane rotation of **M**. Edge-on attachment of a second in-plane rotating **M** analogous to Fig. 3 (C) is prevented by steric hindrance as with **2**N. The results with **2N** and **2M** leave no doubt that in contrast to the previous [3] conclusions phenanthrene and pyrene also form only 1:1 complexes resembling **2N** in topology. The pyrene complex is strong enough to make the disturbance by internal TMS insignificant and to give the expected order of a_2 values [3].

Removal of one ortho-nitro group from **2** reduces the molecular symmetry, increases the conformational flexibility of CH_2COMe and weakens polar effects making complexes of **3** (Fig. 1,

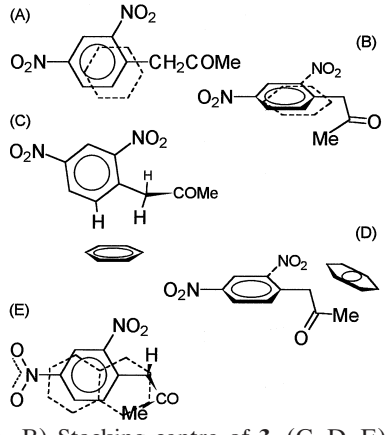

Fig. 4. (A, B) Stacking centre of **3**, (C, D, E) approximate complex topologies for **3**.

Table 2) weaker than those of **2**. The stacking centre of **2** is near the centre of its picryl moiety and is certainly equidistant to the ring protons, that one of **3** is moved away from the 1,4-diagonal (between carbons 1 and 4) of the phenyl ring (Fig. 4: A) as shown below. **3** easily takes on any CH_2COMe conformation as long as the oxygens of CO and NO_2 do not come close to each other. Complexing, however, may select a certain conformation so that polar effects and dispersion forces are optimized. This idea of a selected or perhaps even forced conformation seems to be novel in the field of weak complexes. There is no indication for a ternary complex with **3**.

Complex **3N** is discussed first (Fig. 4: E). The complex centre is near C-6 as shown by the *IK* sequence 6-H > 5-H > CH_2. The last two have certainly been lowered by impeded torsional vibration of 4-NO_2 (5-H) and of 2-NO_2 (rather small influence on *IK* of CH_2); this hindrance is probably more effective for 4-NO_2 than for 2-NO_2. The low *IK* of 3-H is in accord with the relatively large distance to the complex centre and with impeded vibrations of both NO_2. Fig. 4 (E) takes also two details into account. First, only one H of CH_2 is near **N** reducing the joint *IK* of CH_2. Second, in this conformation Me is shielded by **N** but is put into the deshielding plane of dinitrophenyl making *IK* small. The joint polar effects of CH and Me are optimized in this conformation and even the CO dipole is favourably adjusted so that the stacking **N** simultaneously can complex with CHCOMe in an edge-on manner.

3B (Table 2) yielded the same *K* from four of the five proton sites; the deviation for Me is moderate but requires an explanation. The largest *IK* of **3B** is that one of 6-H followed by CH_2 and 5-H again suggesting a stacking centre near 6-C although *IK* of CH_2 is too high as compared to **3N**. A marked polar interaction of **B** with CH_2 seems to be essential for this stacking centre since for the related compound **4** (Fig. 1) a rather centralized stacking has been reported [1] together with some edge-on complex standing with 5-H and 6-H on **B**. A similar isomeric edge-on complex can be expected for **3B** but **3** will stand with 6-H and one H of CH_2 on **B** (Fig. 4: C). This edge-on **3B** is probably stronger than that one of **4** (dipole moment 3.0–3.31 debye) [1] as follows from the dipole moment of 2,4-dinitrotoluene (4.33–4.38 debye) [17]. The small *K* for this edge-on **3B** adds to *K* of the stacking complex for all proton sites except for Me providing a smaller total *K* for Me as found. This appears more reasonable than a ternary complex which influences only one of the five signals. With **3N** $K_{stacking}$ is strong enough to make $K_{edge\text{-}on}$ insignificant (*cf.* **4B** and **4T** in [1]). The total *K*s of **3B** and of **4B** (Table 2) are well comparable while, ignoring CH_2COMe, the *IK* values of **3B** are lower than those of **4B**, distinctly lower for 3-H due to the centralized topology [1] of the stacking **4B**. Contributions to *IK* by edge-on **3B** primarily depend on the distance between the proton and the centre of the complexing **B**. The resulting shielding by **B** is highest for 6-H and one H of CH_2. It decreases in the sequence 5-H >> 3-H > Me. The stacking **B** is too small to cover Me analogously to **3N** (Fig. 4: E) so that this direct shielding of Me by **B** in both isomeric **3B** is small in contrast to the mediocre *IK* in Table 2. But both **3B** may have Me put rather beneath dinitrophenyl as shown for stacking **3B** in Fig. 4 (B) resulting in some intramolecular shielding for both. This shielding by picryl in stacking **3B** would be increased by **B** (two stacking rings in analogy to shielding by $\mathbf{T_2}$; *cf.* **2N**). In stacking **3B** this conformation enables an optimal polar interaction of CH_2 with 2-NO_2. Part of the relatively high *IK* of Me (and partially of CH_2) may also come of an edge-on complex over CH_2COMe (Fig. 4: D). A ternary stacking plus edge-on complex of type **2BB** is prevented by **B** of stacking **3B** due to the complex centre (Fig. 4: A).

The centralized stacking for complexes of **4** probably results from repulsion of D by the four O and from attraction of D by the two N and the proton between them. In chloronitropyridine (**5**) (Fig. 1) **5** (Table 2) one CNO_2 of **4** with its peripheral negative charges is replaced by a ring N providing a much more central negative charge. This shifts the complex centre near C-5, *i.e.* most remote from the ring N both for **5M** (Fig. 5: A) and **5N** (Fig. 5: B) as is evident from the *IK* values of both complexes even if *IK* for 6-H of **5M** might be less reliable than usual owing to partial signal overlap of 6-H and **M**. *IK* values are greatest for 5-H and smallest for 3-H (next to ring N). The latter *IK* is nearly equal in both complexes due to hindrance of NO_2 vibration by **N** and lack of hindrance in **5M** since in-plane rotation of **M** will be prevented by polar interactions of two methyl groups with negative partial charges in **5** (Fig. 5:

A). The *IK* difference between 6-H and 5-H coming of the distance from the centre of D is a bit greater in **5M** then in **5N** since **N** covers 6-H better than **M** does (Fig. 5: A,B).

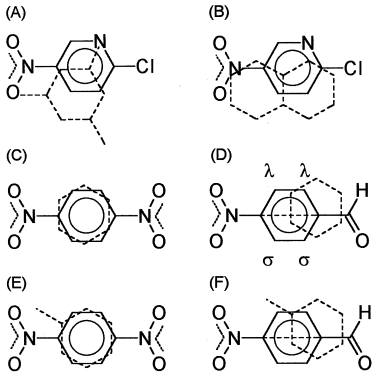

Fig. 5. (A, B) Complexes **5M** and **5N**, (C) complex centre of **7**, (D) complex centre of **6** and unequal shielding of proton pairs in **6**, (E,F) molecular dimensions for dipole-dipole interactions of **T** with **7** and **6**.

Diamagnetic shielding in complexes of 1,4-dinitrobenzene (7) *and of 4-nitrobenzaldehyde* (6)*; unequal shielding in isochronous proton pairs*

The highest 10^2 *IK* (186 ppm) [4] of a stacking **B** complex was found with **7** (Fig. 1). This value is distintly higher than 10^2 *IK* values of **6B** both for meta and for ortho protons (Table 1). In contrast to **6** (Fig. 5: D) [1] the complex centre of **7** should be the centre of this molecule (Fig. 5: C). This can be confirmed as follows. **6** associates both with **T** and $\mathbf{T_2}$ (high *IK*, see above) but **7** cannot form $\mathbf{7T_2}$ since the postulated complex centre enables a dipole-dipole attraction (Fig. 5: E) that stabilizes **7T** and destabilizes $\mathbf{7T_2}$ (stacking of three dipoles, *cf.* [1]); no such attraction is possible in **6T** (Fig. 5: F). Indeed, *IK* of **7T** (Table 2) is insignificantly higher than *IK* of **7B**. The difference of 2% is near the methodical limit but a small increase of diamagnetic shielding may even be expected from the diamagnetic anisotropies [7] of **T** and **B**. Dipole-dipole attraction makes **7T** a stronger complex than **7B** (K = 0.130 M^{-1}) [4] while **6T** is weaker than **6B** (Table 1) since the repulsive action of the vibrating NO_2 is increased by Me of in-plane rotating **T**. This rotation is prevented in **7T**. A different torsional behaviour of NO_2 groups in free **6** and **7** can be excluded since the signals of neighbouring protons go downfield on cooling (CCl_4, 25 °C → −15 °C) by 0.043 ppm for **7** and [1] 0.044 ppm for **6**.

All protons of **7** are isochronous both in free **7** and in **7B**; each proton provides the same contribution to *IK*. **B** in **6B** is closer to CHO than to NO_2 making ortho *IK* greater than meta *IK*; but **B** is also moved away from the 1,4-diagonal of the benzene hexagon making shielding of each proton pair unequal (Fig. 5: D). A σ proton is more remote from the centre of **B** than the λ proton. The σ proton contributes to the joint *IK* less than the λ proton does. Shielding of the λ proton and hence its large contribution to the joint *IK* will not change much relative to a topology that has **B** on the 1,4-diagonal. The total result would be a comparatively small joint *IK*. Thus, **6B** and **7B** suggest that *IK* of such proton pairs decreases when the stacking centre is off the 1,4-diagonal. This idea is corroborated by complexes of **2** and **3**. The complex centre is on the 1,4-diagonal for the former and distinctly away from it for the latter (see above). 10^2 *IK* for 3-H and 5-H of **2N** (both 153 ppm) is split into 98 and 184 ppm with **3N** averaging to 141 ppm, *i. e.* less than 10^2 *IK* for **2N** although hindrance of NO_2 vibrations is stronger in **2N** than in **3N**. The same comparison for the **B** complexes gives 154 (**2**) and 133 ppm (average for **3**) but is less reliable since 1:1 stacking is not the only kind of complexing both for **2B** and **3B**.

A σ contribution should be distinctly smaller than *IK* from **B** on the 1,4-diagonal according to the ring current model of Johnson and Bovey [18]: diamagnetic shielding decreases markedly even more than 35 nm above the plane of benzene when the distance to the central axis exceeds the ring radius. On going from 1 to 1.5 ring radii 36 nm above the benzene plane the shielding decreases by 0.27 ppm according to this model; then the contributions to 10^2 *IK* for a $\lambda-\sigma$ pair may easily differ by about 20–30 ppm. At more central positions the shielding difference is smaller, *e. g.* 0.09 ppm on going from 0 to 0.5 ring radii so that the two contributions to 10^2 *IK* of a proton pair insignificantly differ; the difference is zero when the centre of **B** is eactly over the 1,4-diagonal. The non-symmetrical vibration of CHO may furthermore decrease the contribution by the σ proton of the ortho pair in **6B**. It is essential to keep in mind that this reasoning concerns *IK* values, *i. e.* the changes of shifts caused by complexing.

The inherent shift difference of a proton pair in a frozen planar conformation of **6** should be equal for free **6** and for **6B**.

The furan analogue **1** of **6** has no σ protons. Complexes of **1** with **B**, **T** and **N** (Table 1) in contrast to those of **6** have nearly no difference between *IK* values of the ring protons although the complex centres of **1** and **6** (Fig. 5: D) are comparable. From the presence of the proton pairs in **6** one expects *IK* for ring protons to be greater in complexes of **1**. This is observed (Table 1) for protons next to NO_2, *i. e.* 4-H of **1** *vs. meta* protons of **6**. *IK* values for protons next to CHO are even a bit smaller for **1** complexes. Here the effect of unequal shielding in complexes of **6** is overcompensated in complexes of **1** by the different *syn-anti* ratios of free and complexed **1**. Free **1** (mainly ***anti*-1**) will have the 3-H signal at a relatively high field (in *anti*-furfural 0.15 ppm upfield of *syn*-furfural, see above) making the shift difference between total free **1** and total complexed **1** (mainly ***syn*-1**) small. This may be the reason why *IK* values for ring protons next to CHO do not differ much in complexes of **1** and **6** with the same D.

Experimental Section

For procedures, instrument, external reference, further details and computations see [1, 4, 6, 8]. The accuracy of Δ_0 was $\leq$ 0.0016 ppm; temperature was 30.0 ± 0.3 °C; $[A_0]$ was 0.032–0.036 M for **1P**, 0.0632 M for **5M** and 0.0105–0.0222 M for the other complexes. The preparation of n (11–18, 23 for **1B**) 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 a series. Chemicals were used as purchased; **2** and **3** were prepared following described syntheses [3, 19]. The precision of the temperature dependence of shifts (Bruker Avance 300 instrument, internal TMS) 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. Shifts Δ_0 of doublets were taken from the stronger line unless the weaker line had a lower least square sum (SDDQ in the programs); Δ_0 of all lines were used for **1B** and for complexes of **3** and **5**. *K* is the mean of all lines used as described above; *IK* and m_2 are means of the separately found values.

When cooled to −10 °C a 0.15 M solution of **1** in CCl_4 becomes cloudy and shows a second CHO signal 0.40 ppm upfield (new ring signals < 0.1 ppm upfield). Both findings may possibly arise from secretion and self-association of highly polar ***syn*-1**.

[1] H. Stamm, H.-O. Strumm, K.-H. Loebel, H. Jäckel, U. Hoffmanns, S. Bethke, G. Schilling, J. Chem. Soc., Perkin Trans. 2, 2089 (2001) and preceding papers of this series.
[2] R. Foster, Molecular Complexes, vol. 2, chapter 3, Elek Science, London (1974).
[3] J. A. Chudek, R. Foster, D. R. Twiselton, J. Chem. Soc., Perkin 2, 1385 (1983).
[4] W. Lamberty, H. Stamm, J. Stafe, J. Phys. Chem. **87**, 1589 (1983).
[5] H. Stamm, W. Lamberty, J. Stafe, J. Am. Chem. Soc. **102**, 1529 (1980).
[6] H. Stamm, J. Stafe, Z. Naturforsch. **36b**, 1618 (1981).
[7] H. Stamm, H. Jäckel, J. Am. Chem. Soc. **111**, 6544 (1989).
[8] H. Jäckel, H. Stamm, J. Phys. Chem. **94**, 3495 (1990).
[9] J. A. Chudek, R. Foster, D. J. Livingstone, J. Chem. Soc., Faraday Trans.**75**, 1222 (1979).
[10] G. Scatchard, Ann. N. Y. Sci. **51**, 660 (1949); R. Foster, C. A. Fyfe, Trans. Faraday Soc. **61**, 1926 (1965).
[11] C. J. Cresswell, A. L. Allred, J. Phys. Chem. **66**, 1469 (1962); J. Homer, P. J. Huck, J. Chem. Soc. (A), 227 (1968); K. L. Gammon, S. H. Smallcombe, J. H. Richards, J. Am. Chem. Soc. **94**, 4573 (1972).
[12] H. Stamm, W. Lamberty, J. Stafe, Tetrahedron **32**, 2045 (1976).
[13] K.-J. Dahlqvist, S. Forsén, J. Phys. Chem. **69**, 1760, 4062 (1965).
[14] R. J. Abraham, T. M. Siverns, Tetrahedron **28**, 3015 (1972) and lit. cited therein.
[15] B. Roques, S. Combrisson, C. Riche, C. Pascard-Billy, Tetrahedron **26**, 3555 (1970).
[16] R. Foster, Organic Charge-Transfer Complexes, footnote on p. 127, Academic Press, London (1969).
[17] R. C. Cass, H. Spedding, H. D. Springall, J. Chem. Soc. **1957**, 3451.
[18] C. E. Johnson, F. A. Bovey, J. Chem. Phys. **29**, 1012 (1958); isoshielding lines taken from F. A. Bovey, Nuclear Magnetic Resonance, Fig. III-6, Academic Press, New York and London (1969).
[19] W. Borsche, Ber. Dtsch. Chem. Ges. **42**, 601 (1909).