

A coupled dual hydrogen bridge system—solution dynamics and crystal structure of 2-dimethylamino-4,6-bis(2-hydroxyphenyl)-1,3,5-triazine †

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Peter Fischer,^{*a} Achim Fettig,^a Wolfgang U. Frey,^a Sonja Henkel,^a Helga Hoier,^a Horst E. A. Kramer,^{*b} Manfred Roessler^b and Jean-Luc Birbaum^c

^a Institut für Organische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart, Germany

^b Institut für Physikalische Chemie, Universität Stuttgart

^c Ciba Specialty Chemicals Inc., Basel, Switzerland

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Detailed NMR analysis (CD₂Cl₂, 183 K) shows the two intramolecular hydrogen bridges of 2-dimethylamino-4,6-bis(2-hydroxyphenyl)-1,3,5-triazine to be directed either towards N-1 and N-3 (S conformer; both hydrogen bonds to an aza nitrogen *ortho* to the N(CH₃)₂ group) or towards N-1/N-3, respectively, and N-5 (A conformer; one *ortho* and one *para* hydrogen bond each), with the ratio S:A = 1:2.6₅. The conformational equilibrium has been probed by dynamic NMR spectroscopy. For 180° rotation of one 2-hydroxyphenyl moiety, *i.e.* the mutual interconversion of A and S, $\Delta G^\ddagger \cong 47 \text{ kJ mol}^{-1}$ is determined by complete line shape analysis (range 213–243 K). The activation barrier for simultaneous rotation of both 2-hydroxyphenyl groups is higher by only $\cong 0.5 \text{ kJ mol}^{-1}$; this process thence contributes substantially to the overall dynamic process. For the crystalline state, X-ray diffraction shows only the A conformer. The C–O–H bond angles appear compressed towards 90° for both the *ortho* and the *para* bridge. In the *para* bridge, O(15)–H(15)⋯N(5), the bonding hydrogen is located close to symmetrically between the donor O and the acceptor N (bond angle $\sim 165^\circ$).

Introduction

UV Absorbers with a strong intramolecular hydrogen bond (IMHB) are among the most effective additives for protecting synthetic polymers against photodegradation.^{1,2} Photoexcitation of these molecules is followed by an excited state intramolecular proton transfer (ESIPT) and subsequent rapid radiationless deactivation (which may also be a competitive mode).^{3,4} The ESIPT process itself constitutes no absolute prerequisite for effective energy transformation. The proviso rather is conservation of the IMHB in the excited state to offer a sufficiently wide range of vibrational modes for triggering radiationless deactivation;⁵ the strength of the hydrogen bond therefore is of crucial importance.

A comparative X-ray structure analysis as well as IR and NMR spectral evidence have demonstrated that the IMHB in 2-hydroxyaryltriazines is far stronger than that in the corresponding 2-hydroxyarylbenzotriazoles (*e.g.* Tinuvin P®).⁶ Breaking the hydrogen bridge in 2,4-bis(2,4-dimethylphenyl)-6-(2-hydroxy-4-methoxyphenyl)-1,3,5-triazine, for instance, requires an enthalpy of activation $\Delta H^\ddagger = 50 \text{ kJ mol}^{-1}$ as we have determined by dynamic NMR spectroscopy.⁷ Yet even these strong, chelate-type bonds can be opened *in the excited state* by sufficiently polar matrices such as polymethacrylate coatings.⁸ It seemed conceivable, though, that in a triazine with a second IMHB, this would stay intact even under these conditions and furnish the requisite vibrational modes.

We now report on assessing, both quantitatively and individually, the strength of the two hydrogen bonds in such a dual-bridge triazine system.

Results and discussion

NMR Study of solution dynamics

2-Dimethylamino-4,6-bis(2-hydroxyphenyl)-1,3,5-triazine, a new representative in the class of (2-hydroxyaryl)triazines, indeed forms *two* intramolecular hydrogen bridges *at the same time*. With the reasonable assumption that none of the aza nitrogen atoms in the triazine ring may function as an acceptor for two bridges simultaneously, three arrangements are possible for these two hydrogen bonds: one conformation with C₂ symmetry (S in Fig. 1), and two asymmetrical conformations (A', A'') which are transformed into one other by 180° rotation around the C₂ axis, and thence are structurally identical and energetically degenerate.

The two asymmetrical conformations A' and A'' are converted, by 180° rotation around the C-4–C-1' or C-6–C-1'' bond, respectively, into the symmetrical structure S which in turn is transformed, by a 180° rotation around the C-6–C-1'' or C-4–C-1' bond, into the respective other asymmetrical conformer. Simultaneous rotation, finally, around both the C-4–C-1' and the C-6–C-1'' bond directly interconverts A' and A''. All these transformations constitute equilibria with first order forward and back reactions which are characterized by six rate constants as assigned in Fig. 1.

Hydrogen bridging conformers. The structural identity of A' and A'' might tempt one to describe the system on the basis of *two* conformations only, with the asymmetrical one assuming double weight. As demonstrated in Fig. 1, *three* different chemical environments exist, though, for each of the bridging protons, and conformers A' and A'' thus represent distinctly different sites for a *given* bridging proton. An expansion of the ¹H spectrum at 183 K (Fig. 2a), where the dynamic process is frozen out on the NMR time scale, indeed shows

† A stereoscopic projection of the packing of the crystal structure of 2-dimethylamino-4,6-bis(2-hydroxyphenyl)-1,3,5-triazine is available as supplementary data. For direct electronic access see <http://www.rsc.org/suppdata/p2/b0/b005956k/>

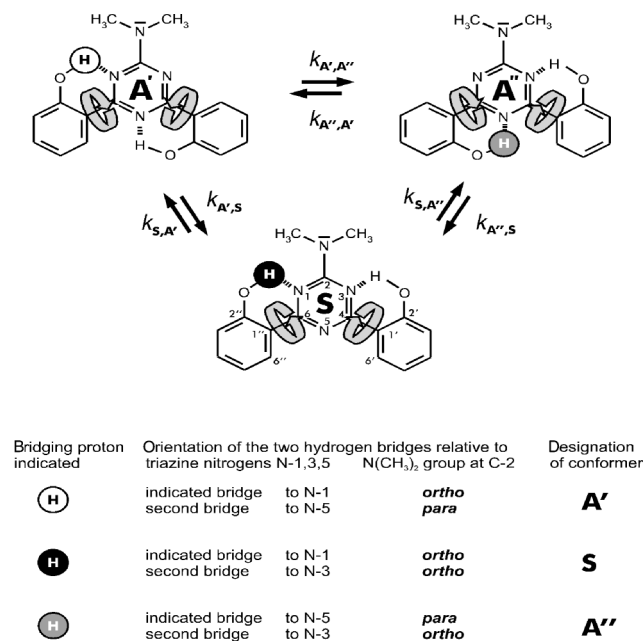


Fig. 1 Reaction scheme for the interconversion of the two O–H···N hydrogen bridges in 2-dimethylamino-4,6-bis(2-hydroxyphenyl)-1,3,5-triazine, based on the “three site exchange” model, for the phenolic proton of the left-hand 2-hydroxyphenyl ring.

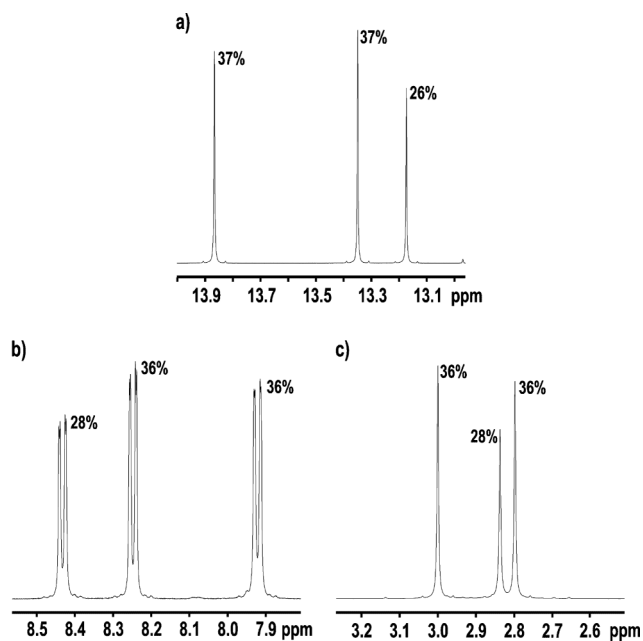


Fig. 2 ¹H NMR spectrum of 2-dimethylamino-4,6-bis(2-hydroxyphenyl)-1,3,5-triazine at 183 K (11.74 T, CD₂Cl₂); expansions for a) the O–H···N bridging protons, b) 6',6''-H, c) the *syn* and *anti* N-CH₃ groups of the dimethylamino function.

three singlets in the low field region ($\delta > 13$ ppm), one for each of the *three bridging sites* (isochronous, of course, for the *two bridging protons*), with a relative intensity of 37, 37, and 26% (calculated as percentages of the integral over all three signals).

Two singlets with different chemical shifts, though equal intensity, are expected for the *ortho* and the *para* bridge, respectively, of the symmetry-equivalent conformers A' and A''. The two more intense (37%) resonances thence can be unequivocally assigned to the asymmetrical form. The bridging protons in the symmetrical S conformer are in chemically identical environments and so give rise to the remaining, less intense (26%) singlet. The same arguments hold for all atom positions in this

triazine. The aryl protons 6',6''-H, for instance, in the *ortho* position opposite to the bridging hydroxy groups, are set off to low field due to the combined –M and anisotropy effect of the triazine ring. The expansion in Fig. 2b shows that their resonances are likewise split into three multiplets (relative intensity 36/36/28%; $^3J(6'-H,5'-H) = 7.9$ Hz, $^4J(6'-H,4'-H) = 1.2$ Hz).

Three singlets, with once more the same intensity ratio, also appear for the N(CH₃)₂ protons (*cf.* Fig. 2c; relative intensity again 28/36/36%). The C–N bond, by which the +M substituent N(CH₃)₂ is joined to the triazine ring, has considerable partial double bond character. At 183 K, rotation around this bond is completely frozen out as we have unequivocally established for the homologous 2-dimethylamino-4-(2-hydroxyphenyl)-6-phenyl-1,3,5-triazine.⁹ This holds up to >323 K,⁹ *i.e.* the barrier of rotation for the N(CH₃)₂ moiety in 2-dimethylamino-4,6-bis(2-hydroxyphenyl)-1,3,5-triazine has the same order of magnitude as in dimethylformamide.¹⁰ For both asymmetrical conformers A' and A'', two signals therefore are expected, at all temperatures investigated here, for the two N-CH₃ groups, oriented *syn* and *anti*, respectively, to the *ortho* hydrogen bridge, and mutually isochronous for the two forms. The third, less intense singlet arises from the symmetry-equivalent N-CH₃ groups of the S conformer.

On this compound NMR evidence, the two structures with both an *ortho* and a *para* bridge appear favoured over the conformer with two *ortho* bridges by 2.6₅:1. Since a (partial) positive charge is stabilized by a +M substituent in the *para* better than in the *ortho* position, the slight preference for an O–H···N bridge to the aza nitrogen *para* to the N(CH₃)₂ group appears quite reasonable. The somewhat greater strength of this O–H···N bridge also implies a higher energy of activation for breaking a *para* than for disrupting an *ortho* hydrogen bond. The schematic energy diagram in Fig. 3 rests on this reasonable assumption.

Determination of interconversion rate constants by NMR line shape analysis. The dynamic process, underlying the interconversion of the individual conformers, is best studied by dynamic NMR spectroscopy (DNMR).^{11–13} With a liquidus range from –96 to +40 °C, CD₂Cl₂ is ideally suited for following the dynamic process from the slow-exchange limit to the stage of a single coalesced signal. Expansions of the ¹H spectrum with the N-CH₃ signal(s) at three different temperatures are displayed in Fig. 4. As discussed above, there are three well-defined singlets at 183 K (*cf.* Fig. 2c). At 213 K, the two signals at 2.8 ppm have already merged. For the one broad resonance, remaining at 233 K, only the hump on the low-field flank indicates that this is in fact a threefold coalescing signal.

With such a complex pattern, coalescence points can no longer be accurately fixed as for the other (2-hydroxyaryl)-triazines studied so far.^{7,9} Rate constants for the individual transformations rather must be determined by complete line shape analysis^{14,15} requiring, besides precise frequency position and half-height width of the individual signals at a given temperature, the molar fraction(s) *p* of the corresponding conformer(s). These were determined by separate integration over the 6',6''-H signals for the individual conformers, and remain constant, within the NMR integration error limit, between 183 and 213 K when increasing signal overlap thwarts sufficiently precise separate integration.

$$p_{A'} = p_{A''} = 0.35_7$$

$$p_S = 0.28_6$$

The individual transformation rates, as assigned in Fig. 1, are intercorrelated by these molar fractions as shown in eqn. (1) and (2):

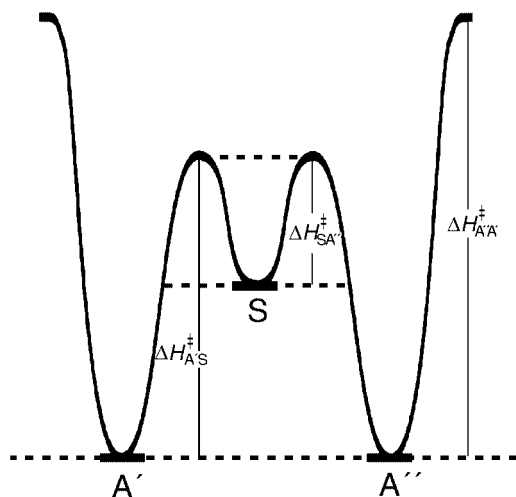


Fig. 3 Schematic energy diagram for the interconversion of the A', S and A'' conformers.

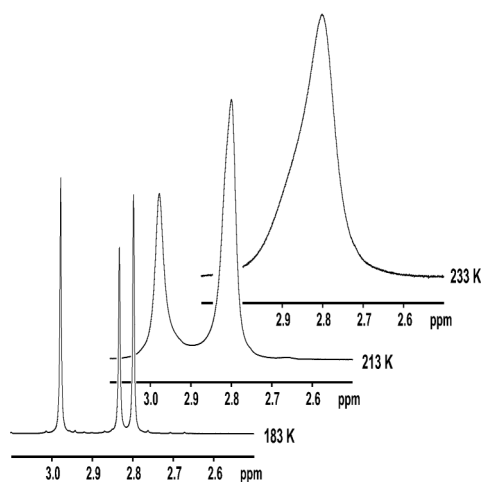


Fig. 4 $N\text{-CH}_3$ ^1H resonances of 2-dimethylamino-4,6-bis(2-hydroxyphenyl)-1,3,5-triazine at 183, 213, and 233 K (11.74 T, CD_2Cl_2).

$$k_{A'/S} = (p_S/p_{A'}) \cdot k_{S/A'} = k_{A''/S} = (p_S/p_{A''}) \cdot k_{S/A''} \quad (1)$$

$$k_{A'/A''} = k_{A''/A'} \quad (2)$$

The six principal rate constants of the “three-site exchange” model (*cf.* Fig. 1) in practice thus are reduced to two; these we have varied, systematically, for a best fit between calculated and experimental line shape. Rotation around the (C-2)- $\text{N}(\text{CH}_3)_2$ bond is frozen out in the temperature range in question,⁹ as stated above, and thence need not be considered for the exchange. Fig. 5a shows, exemplarily, the close to perfect fit for the $N\text{-CH}_3$ resonances at 213 and 228 K, *i.e.* at temperatures somewhat below coalescence: the experimental spectral trace always lies centered in the grey-shaded band which represents the calculated spectrum. The 6',6''-H resonances have only one third the relative intensity of the $N\text{-CH}_3$ signal, and are further split by $^1\text{H}, ^1\text{H}$ coupling. Despite the far lower signal to noise ratio, especially above 223 K, an excellent fit is still obtained as demonstrated in Fig. 5b. For the bridging proton signals, on the other hand, a line shape analysis is not practical. Due perhaps to increasing alignment of CD_2Cl_2 solvent dipoles with the hydrogen bridge dipoles at lower temperatures, the line width of these resonances is itself strongly temperature-dependent. The half-height width, determined from a slow-exchange spectrum, thus cannot be used for simulations at higher temperatures.

Activation parameters for interconversion of the bridging conformers. The rate constants, obtained from the various line fit analyses, are collected in Table 1. If they are plotted *vs.* $1/T$,

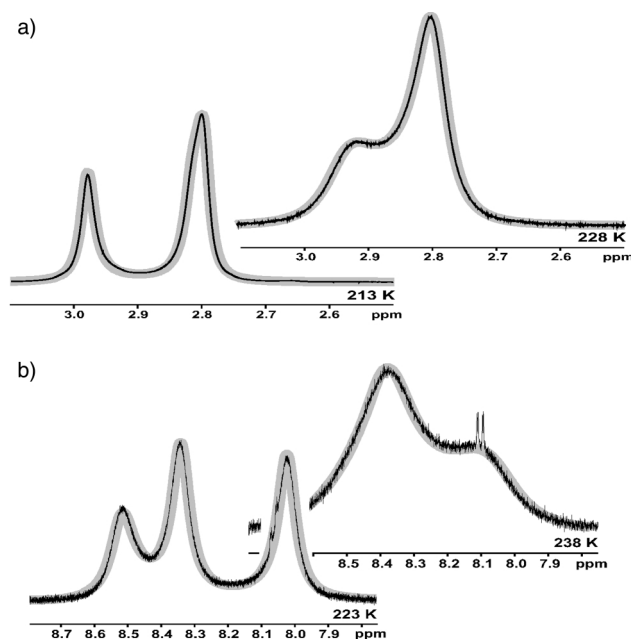


Fig. 5 Line shape analysis for the ^1H resonances (11.74 T, CD_2Cl_2) of 2-dimethylamino-4,6-bis(2-hydroxyphenyl)-1,3,5-triazine: black trace—experimental spectrum, grey-shaded band—calculated line shape for the best fit of the two iterated rate constants. a) $N\text{-CH}_3$ signals at 213 and 228 K, b) 6',6''-H signals at 223 and 238 K.

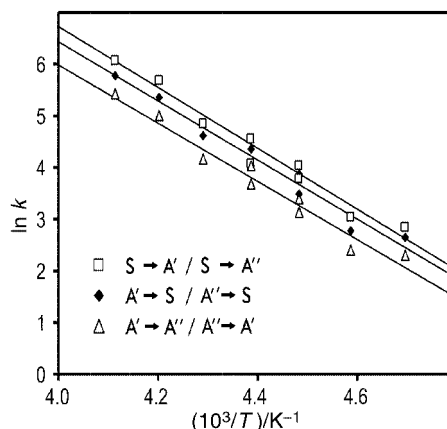


Fig. 6 Arrhenius plot for the individual hydrogen bridge interconversions in 2-dimethylamino-4,6-bis(2-hydroxyphenyl)-1,3,5-triazine (for data *cf.* Table 1).

either as $\log(k/T)$ in an Eyring, or as $\ln k$ in an Arrhenius diagram (Fig. 6),¹⁰ linear regression analysis yields individual activation parameters for each hydrogen bridge re-orientation. The values for energy and enthalpy of activation appear as identical, though, for all transformations within the rather wide error limits (Table 2).

Alternatively, ΔG^\ddagger values can be calculated directly from the k values for each temperature (*cf.* Table 1). If these are plotted *vs.* T in a Gibbs–Helmholtz diagram, the error in the k/T or, respectively, $\Delta G^\ddagger/T$ correlations is smaller by more than an order of magnitude within the temperature range for which the individual k values were determined experimentally by line shape analysis (213–243 K). This is demonstrated strikingly in Fig. 7 for the two interconversions $\text{S} \rightarrow \text{A}'/\text{S} \rightarrow \text{A}''$. The 6',6''-H and $N\text{-CH}_3$ signals have been evaluated jointly for this correlation; still, over a range of 30 K, the correlation straight line lies well within the error bars for the individual ΔG^\ddagger values, with purely statistical deviations.

Closer inspection of the $\Delta G^\ddagger/T$ correlation plot in fact reveals a delicate gradation (*cf.* the blow-up in Fig. 8) which is already apparent in the Arrhenius diagram (see Fig. 6). Conformational changes, by which the more stable *para* hydrogen

Table 1 Rate constants and activation parameters for the interconversion of the hydrogen bridging conformers A' , A'' , and S (cf. Fig. 1) of 2-dimethylamino-4,6-bis(2-hydroxyphenyl)-1,3,5-triazine (0.1 M in CD_2Cl_2)

T/K	Position	$k_{A',S} = k_{A'',S}/s^{-1}$	$\Delta G_{A',S}^\ddagger = \Delta G_{A'',S}^\ddagger/kJ mol^{-1}$	$\Delta H^\ddagger/kJ mol^{-1}$
213	N-CH ₃	14	46.9 ± 0.4 ₂	
218	6',6''-H	16	47.8 ± 0.4 ₃	
223	6',6''-H	33	47.6 ± 0.4 ₃	
223	N-CH ₃	48	46.9 ± 0.4 ₃	46 ± 7 ^b
228	6',6''-H	57	47.7 ± 0.4 ₄	(46 ± 3) ^c
228	N-CH ₃	79	47.0 ± 0.4 ₄	
233	6',6''-H	102	47.6 ± 0.4 ₄	
238	6',6''-H	215	47.2 ± 0.4 ₅	
243	6',6''-H	320	47.4 ± 0.4 ₅	

T/K	Position	$k_{S,A'} = k_{S,A''}/s^{-1}$	$\Delta G_{S,A'}^\ddagger = \Delta G_{S,A''}^\ddagger/kJ mol^{-1}$	$\Delta H^\ddagger/kJ mol^{-1}$
213	N-CH ₃	17	46.6 ± 0.4 ₂	
218	6',6''-H	21	47.3 ± 0.4 ₃	
223	6',6''-H	44	47.1 ± 0.4 ₃	
223	N-CH ₃	56	46.6 ± 0.4 ₃	47 ± 7 ^d
228	6',6''-H	58	47.7 ± 0.4 ₄	(47 ± 3) ^c
228	N-CH ₃	95	46.7 ± 0.4 ₄	
233	6',6''-H	125	47.2 ± 0.4 ₄	
238	6',6''-H	288	46.6 ± 0.4 ₅	
243	6',6''-H	428	46.9 ± 0.4 ₅	

T/K	Position	$k_{A',A''} = k_{A'',A'}/s^{-1}$	$\Delta G_{A',A''}^\ddagger = \Delta G_{A'',A'}^\ddagger/kJ mol^{-1}$	$\Delta H^\ddagger/kJ mol^{-1}$
213	N-CH ₃	10	47.5 ± 0.4 ₂	
218	6',6''-H	11	48.4 ± 0.4 ₃	
223	6',6''-H	23	48.3 ± 0.4 ₃	
223	N-CH ₃	30	47.7 ± 0.4 ₃	46 ± 7 ^e
228	6',6''-H	40	48.4 ± 0.4 ₄	(45 ± 3) ^c
228	N-CH ₃	56	47.7 ± 0.4 ₅	
233	6',6''-H	65	48.5 ± 0.4 ₅	
238	6',6''-H	150	47.9 ± 0.4 ₅	
243	6',6''-H	223	48.2 ± 0.4 ₅	

^a Obtained as intercept from a ΔG^\ddagger vs. T plot. ^b The entropy of activation ΔS^\ddagger is obtained from the slope of the respective correlation straight lines: $7 \pm 30 J K^{-1} mol^{-1}$. ^c Obtained as slope from an Eyring plot $\log(k/T)$ vs. $1/T$. ^d The entropy of activation ΔS^\ddagger is obtained from the slope of the respective correlation straight lines: $0 \pm 31 J K^{-1} mol^{-1}$. ^e The entropy of activation ΔS^\ddagger is obtained from the slope of the respective correlation straight lines: $10 \pm 30 J K^{-1} mol^{-1}$.

Table 2 Activation energy and enthalpy of activation for the three interconversion processes obtained, respectively, from the slope of a $\ln k$ or a $\log(k/T)$ vs. $1/T$ correlation

Interconversion	$E_A/kJ mol^{-1}$	$\Delta H^\ddagger/kJ mol^{-1}$
$S \rightarrow A'/S \rightarrow A''$	48 ± 3	47 ± 3
$A' \rightarrow S/A'' \rightarrow S$	47 ± 3	46 ± 3
$A' \rightarrow A''/A'' \rightarrow A'$	47 ± 3	45 ± 3

bridge is formed, as expected require a slightly lower activation energy than processes during which such a *para* bridge is broken, *i.e.* the correlation straight line for the transformations $A' \rightarrow S/A'' \rightarrow S$ is set off by $\sim 0.5 kJ mol^{-1}$ from that for the reverse processes. The free enthalpy difference between symmetrical and asymmetrical conformer at *e.g.* 238 K is calculated from the A/S ratio at this temperature as $\Delta\Delta G = 0.67 kJ mol^{-1}$. The free enthalpies of activation ΔG^\ddagger for the forward and back reaction, *i.e.* the transformations $A' \rightarrow S$ and $S \rightarrow A'$ and likewise $A'' \rightarrow S$ and $S \rightarrow A''$ must differ by the same value independent of how high the activation barrier is (cf. Fig. 3). Agreement between the values for $\Delta\Delta G$, derived from thermodynamic, and $\Delta\Delta G^\ddagger$, derived from kinetic data, is more than satisfactory.

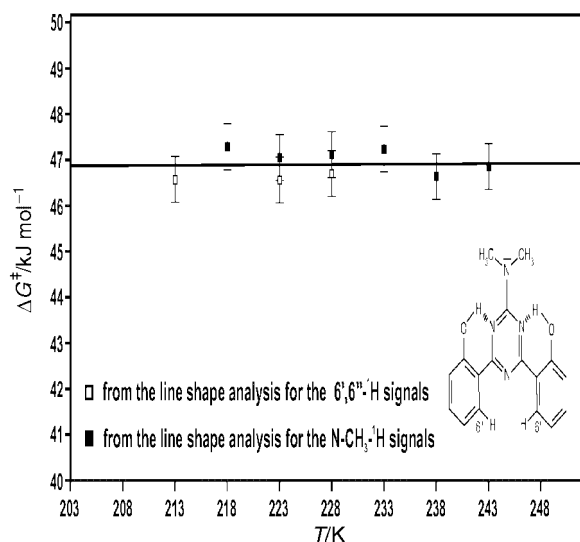


Fig. 7 $\Delta G^\ddagger/T$ Correlation for the transformations $S \rightarrow A'$ and $S \rightarrow A''$.

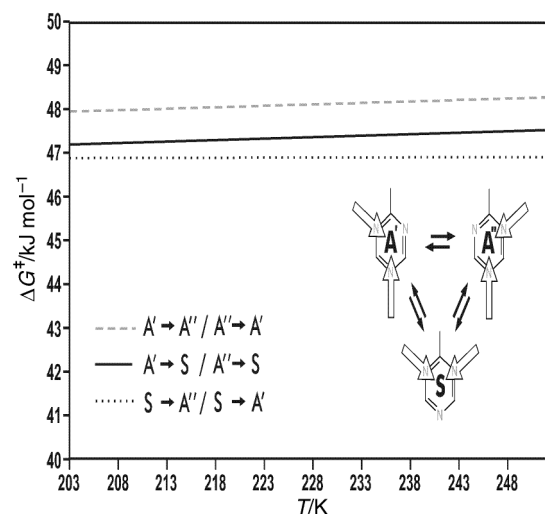


Fig. 8 $\Delta G^\ddagger/T$ Correlation straight lines for the individual hydrogen bridge interconversions in 2-dimethylamino-4,6-bis(2-hydroxyphenyl)-1,3,5-triazine.

Direct interconversion of A' and A'' requires sacrificing both hydrogen bonds at the same time, and therefore appears *a priori* rather unlikely. The perfect line shape fit, as is demonstrated exemplarily in Figs. 5a,b, can be obtained, however, only when the two rate constants for this process, $k_{A',A''}$ and $k_{A'',A'}$, are included in the simulation. Even more surprisingly, the double bridge exchange is barely slower than the other two re-orientation processes where only *one* hydrogen bridge needs to be broken, and thence contributes significantly and substantially to the dynamic process. The activation barrier, determined by DNMR, for the $A' \rightleftharpoons A''$ interconversion as a matter of fact again lies only $\sim 0.5 kJ mol^{-1}$ higher than that for the *para* \rightarrow *ortho* rearrangement ($A' \rightarrow S/A'' \rightarrow S$; cf. Figs. 6 and 8).

X-Ray crystal structure determination ‡

2-Dimethylamino-4,6-bis(2-hydroxyphenyl)-1,3,5-triazine crystallizes in the monoclinic space group $P2_1/c$, with one molecule per asymmetric unit (for selected bond lengths and angles, see Table 3; fractional atomic coordinates, stereoscopic projections of crystal packing, and other relevant crystallographic data are available as supplementary data ‡). The arrangement in the

‡ CCDC reference number 188/280. See <http://www.rsc.org/suppdata/p2/b0/b005956k/> for crystallographic files in .cif format.

Table 3 Selected bond lengths (Å) and angles (°) for 2-dimethylamino-4,6-bis(2-hydroxyphenyl)-1,3,5-triazine (*cf.* Fig. 10; esds in parentheses)

C(2)–N(1)	1.350(4)	C(2)–N(7)	1.332(4)
C(2)–N(3)	1.351(4)	N(7)–C(8)	1.457(4)
N(1)–C(6)	1.333(4)	N(7)–C(9)	1.457(4)
N(3)–C(4)	1.330(4)		
N(5)–C(6)	1.343(4)		
N(5)–C(4)	1.346(4)		
C(4)–C(10)	1.480(4)	C(6)–C(16)	1.469(4)
C(10)–C(15)	1.395(5)	C(16)–C(21)	1.406(4)
C(15)–O(15)	1.304(4)	C(21)–O(21)	1.334(4)
O(15)–H(15)	1.25(7)	O(21)–H(21)	0.97(6)
H(15)⋯N(5)	1.35(7)	H(21)⋯N(1)	1.66(6)
O(15)⋯N(5)	2.561(4)	O(21)⋯N(1)	2.574(3)
N(5)–C(4)–C(10)	117.1(3)	N(1)–C(6)–C(16)	117.9(3)
C(4)–C(10)–C(15)	122.2(3)	C(6)–C(16)–C(21)	121.9(3)
C(10)–C(15)–O(15)	122.5(3)	C(16)–O(21)–H(21)	122.8(3)
C(15)–O(15)–H(15)	97(3)	C(21)–O(21)–H(21)	103(3)
O(15)–H(15)–N(5)	160(5)	O(21)–H(21)–N(1)	154(5)

unit cell ($Z = 4$) is much like that for an analogue without an IMHB, 2-(4-methoxy)-4,6-diphenyl-1,3,5-triazine.⁶

The packing diagram (Fig. 9a) shows perfectly planar bis(hydroxyphenyl)triazines, arranged in oblique stacks which are tilted relative to each other by $\sim 30^\circ$ in a herring-bone-like arrangement. The crystal structure gives no indication, either of interaction between the individual stacks or of intermolecular hydrogen bridging, orthogonal to the plane of the triazines, within the stacks. Charge-transfer between two adjacent layers is likewise precluded by the vertical separation of the molecules within a stack (3.6–3.8 Å) as well as by their relative orientation. For an effective charge-transfer, the electron-deficient triazine core would have to be oriented face to face over one of the electron-rich hydroxyphenyl rings in an adjacent layer; as the projection in Fig. 9b clearly shows, this is not the case. Another cooperative effect becomes apparent, though, from this representation of the crystal ordering: within the stacks, the triazines are arranged pairwise, with the strong $N(\text{CH}_3)_2$ donors diametrically opposite, and the overall molecular dipole moments thus compensating each other for any such pair. The two triazines of a pair are displaced sideways by only half a triazine diameter to minimize steric interactions; the triazine in the next layer, however, which belongs to another dipole-compensated pair, is displaced by one and a half triazine diameters.

The structure gives no indication of disorder: only the slightly more stable asymmetrical conformer **A**, with one *ortho* and *para* hydrogen bridge each, is represented in the crystal (**A'** and **A''** are of course crystallographically symmetry-equivalent). The Boltzmann energy, available at the (ambient) temperature at which the structure was determined, is insufficient for reorientation of these intramolecular hydrogen bonds. Another striking element of order becomes apparent, though, if one assigns the acceptor site for the *ortho* hydrogen bridge as N-3, and that for the *para* bridge as N-5: all triazines in the crystal show the same sense of rotation.

A strong molecular dipole moment had been invoked above to rationalize the pairwise head-to-tail alignment of the triazine moieties within the vertical stacks. The attenuated bond length between C-2 and the dimethylamino nitrogen N-7 and also the negligible torsional angle (1.332 Å and 0.5° , respectively; *cf.* Table 3 and Fig. 10) likewise prove an exceptionally strong mesomeric interaction between the $(\text{CH}_3)_2\text{N}$ group as +M donor and the triazine π system as acceptor. This manifests itself most strikingly in the fact that the formal single bond N(7)–C(2) has the same length, within the standard deviation of the X-ray analysis, as the two aromatic N(1)–C(6) and N(3)–C(4) bonds (1.332 *vs.* 1.333 and 1.330 Å). Since the six C–N bonds within the triazine core, on the other hand, all have more

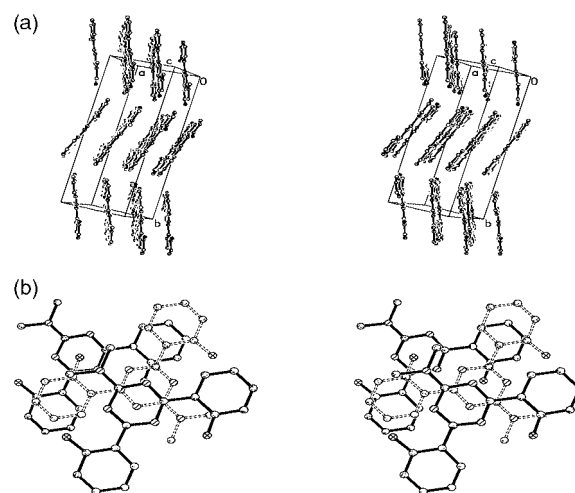


Fig. 9 3D Packing diagram with unit cell dimensions for 2-dimethylamino-4,6-bis(2-hydroxyphenyl)-1,3,5-triazine: a) viewed along the triazine σ plane, b) three successive molecules within a stack (the middle one drawn with dashed lines).

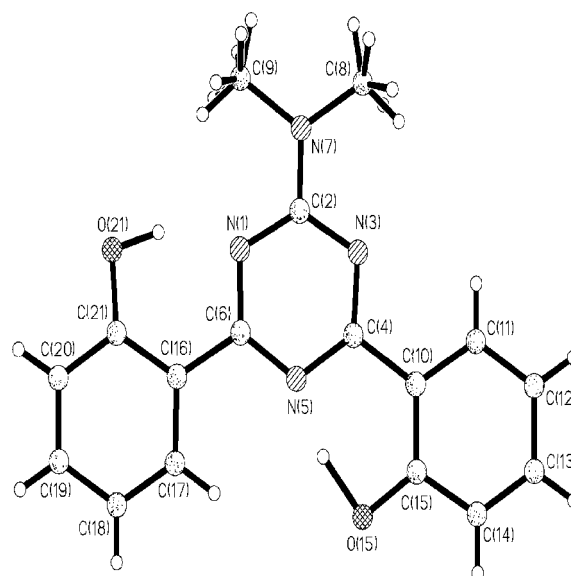


Fig. 10 X-Ray crystal structure for 2-dimethylamino-4,6-bis(2-hydroxyphenyl)-1,3,5-triazine (**A** conformer only) with atom labelling.

or less identical length (1.34 ± 0.01 Å), this must be interpreted in terms of a (charge-transfer) polarization of the π -electron cloud as a whole,¹⁶ apparently a class characteristic of these aryltriazines,¹⁷ rather than in terms of a *para*-quinoid structure which would require strictly alternating bond lengths. The crystal structure data thus present a perfect rationale for why rotation around the C(2)–N(7) bond is frozen out even in ambient temperature NMR spectra (see above).

The position of the bridging hydrogen could be refined for both the *ortho* and the *para* bridge (*cf.* Experimental section). Compared to the single bridge in 2-(2-hydroxy-4-methoxyphenyl)-4,6-diphenyl-1,3,5-triazine (M–OH–P),⁶ the O–H bond of the *ortho* hydrogen bridge, O(21)–H(21)⋯N(1), in 2-dimethylamino-4,6-bis(2-hydroxyphenyl)-1,3,5-triazine (NMe₂) appears even more elongated (0.97 *vs.* 0.898 Å, see Table 4), with a concomitant reduction in the N⋯H distance, and the C(21)–O(21) bond even more compressed. The O–H⋯N inter-hydrogen-bond angle, though, deviates markedly further from linear than in M–OH–P.

The C(15)–O(15) bond and the overall O–H⋯N distance of the *para* bridge both are shortened still further, and the O–H⋯N inter-hydrogen-bond angle is flattened out again

Table 4 Structural parameters for the intramolecular hydrogen bridges in two different (2-hydroxyaryl)triazines

	<i>r</i> /Å	C–O	O–H	H···N	O–H···N	O–H···N/°	(O–H···N)/°
M–OH–P ⁶	Single bridge	1.368	0.898	1.733	2.594	159.6	
NMe ₂	<i>ortho</i> bridge	1.334	0.97	1.66	2.574	154	
	<i>para</i> bridge	1.304	1.25	1.35	2.561	160	

(160°). The striking difference, though, is in the position of the bridging hydrogen which is located almost intermediate between O(15) and N(5): at least in the crystalline state, the hydrogen bridge O(15)–H(15)···N(5) seems to approach the symmetrical (Table 4).

Conclusion

In conjunction, the NMR and crystal structure, *i.e.* solution and solid state data presented here constitute clear proof that *both* hydrogen bridges of a bis(2-hydroxyaryl)triazine are at least comparable in strength, individually, to the *single* hydrogen bond in analogous (2-hydroxyaryl)triazines, and thence definitely stronger than the hydrogen bridge in any corresponding benzotriazole.^{6,8}

It has been clearly demonstrated, on the other hand, that the intramolecular hydrogen bond (IMHB) in *e.g.* 2-(2-hydroxy-4-methoxyphenyl)-4,6-diphenyl-1,3,5-triazine must be opened upon irradiation, under formation of an intermolecular hydrogen bond to the solvent lattice, before the triplet state will be populated, with concomitant evolution of phosphorescence.¹⁸ A comparative study of 2-hydroxyaryl- and the corresponding 2-methoxyaryl-triazines, with two, one, and no IMHB, respectively, has furthermore shown that *all* intramolecular bridges must be opened for these molecules to exhibit phosphorescence.¹⁹ With the strength of both bridges now definitely established as comparable, it becomes readily apparent why bis(2-hydroxyaryl)-1,3,5-triazines are distinctly more resistant to photodegradation than structurally corresponding triazines with only one IMHB.

Experimental

DNMR measurements and spectral analysis

¹H NMR spectra were recorded on a Bruker ARX-500 spectrometer (11.74 T, nominal frequency 500.13 MHz, 0.1 M solution in CD₂Cl₂) with the following standard parameters for the individual measurements at a given temperature:^{7,9} pulse width (90°) 11.3 μs, 30° flip angle, 32K FID, digital resolution ±0.16 Hz per point. Temperature was adjusted and controlled by a Bruker BVT-2000 variable temperature unit calibrated according to van Geet.²⁰ To ensure maximum homogeneity after resetting the temperature, the sample was held for 20 min at this temperature in the probehead before acquisition was started.

Complete line shape analyses were performed with a program based on DNMR5.¹⁵ The source program used²¹ was modified for a direct on-screen fit of calculated to experimental trace.⁹ In the range of incipient coalescence, the effective resonance frequency was determined by extrapolation from a Δ*v*/*T* plot for each signal. The highest field resonance within each set was taken as reference, and assigned 0 Hz relative frequency for each temperature. Since the slope in the Δ*v*/*T* plot for a given signal may be positive, negative, or close to zero,^{7,9} the relative Δ*v* values for a given set show no regular trend. The following relative line positions were used for the simulations: *N*-CH₃—0, 90, 250 Hz (218 K); 0, 90, 249 Hz (223 K); 0, 88, 245 Hz (228 K); 0, 85, 237 Hz (233 K); 0, 84, 235 Hz (238 K); 0, 84, 233 Hz (243 K); 6',6''-H—0, 81, 92 Hz (213 K); 0, 70, 83 Hz (223 K); 0, 69, 81 Hz (228 K). A line width of 5 Hz was employed for the

N-CH₃ resonances. For the *ortho*-aryl protons 6',6''-H, this value was incremented by the sum of the two coupling constants, ³*J*_{*ortho*} + ⁴*J*_{*meta*}, giving an effective line width of 14 Hz.

X-Ray analysis

2-Dimethylamino-4,6-bis(2-hydroxyphenyl)-1,3,5-triazine was purified by repeated recrystallization from anhydrous cyclohexane. Yellow crystals were grown from chloroform at ambient temperature by slow solvent evaporation within ten months; residual solvent was removed *in vacuo*. A single crystal (1.2 × 0.45 × 0.2 mm³, mounted in a thin-walled capillary) was used for X-ray data collection on a Nicolet/Siemens P3 four-cycle diffractometer with graphite-monochromatized Mo-Kα radiation (λ = 0.71069 Å). Reflection data were collected to a resolution of 2θ_{max} = 50°, and subjected to a full-matrix least-square refinement without any constraints.

Crystal data. C₁₇H₁₆N₄O₂, *M* = 308.34, monoclinic, *a* = 7.984(1), *b* = 21.589(4), *c* = 8.731(1) Å, β = 90.35(1)°, *U* = 1504.9(4) Å³, 293 K (thermostated), space group *P2₁/c*, *Z* = 4, μ(Mo-Kα) = 0.093 mm⁻¹, 2854 reflexions measured, 2658 unique (*R*_{int} = 0.0123). Of these, 2451 were used for refinement to a final value for *R*₁(*F*) (>2σ(*I*)) = 0.0816 and for ω*R*₂(*F*²) (>2σ(*I*)) = 0.2326.

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