

Prototropic Tautomerism of Tri- and Tetra-phenyl-2,3(2,5)-dihydro-1,3,5-triazines

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Spectroscopic studies (i.r., u.v., and ^1H n.m.r.) of 2,2,4,6-tetraphenyldihydro-1,3,5-triazine (1), and other simple tri- and tetra-phenyldihydro-1,3,5-triazines showed that (1), 2,4,6-triphenyldihydro-1,3,5-triazine (6), and its 2-methyl- (7), and 2-ethyl- (8) derivatives exist in an equilibrium mixture of 2,3-dihydro (a) and 2,5-dihydro (b) forms. From the ratio obtained from the spectra the 2,3-dihydro- (a) form was preferred in (1) and (6)—(8) in solution and in the solid state.

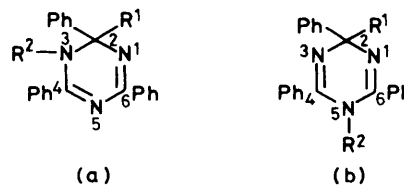
2,2,4,6-Tetraphenyldihydro-1,3,5-triazine (1) was suggested by Lottermoser¹ to exist in the 2,3-dihydro-form, one of the possible tautomers for dihydro-1,3,5-triazines. During the course of an investigation of the photochromism of (1) we found that the i.r. spectrum of a solid sample (KBr pellet) recrystallized from acetone showed two bands at 1 612 (a band), and 1 685 cm^{-1} (b band) with a relative intensity of 3:1; both bands were considered to result from C=N vibrations in the dihydrotriazine ring. The intensity ratio of the a and b bands was found to vary for spectra measured in chloroform solution (a:b = 4:3), or in the solid samples (a:b = 2:1—1:1) which remained after evaporation of solvents from several solutions (n-hexane, benzene, acetone, dichloromethane, and dioxane) of (1). These findings suggested that compound (1) is a mixture of two interconvertible compounds, presumably the tautomers, 2,2,4,6-tetraphenyl-2,3-dihydro-1,3,5-triazine (1a), and 2,2,4,6-tetraphenyl-2,5-dihydro-1,3,5-triazine (1b). The two C=N bands at 1 612 and 1 685 cm^{-1} in the i.r. spectrum of (1) were tentatively assigned to the stretching modes of the $-\text{N}=\text{C}-\text{N}=\text{C}-\text{NH}-$ and $-\text{N}=\text{C}-\text{NH}-\text{C}=\text{N}-$ fragments in (1a) and (1b), respectively.

In order to confirm this assignment, dihydrotriazines (2)—(9) were prepared and the wavenumbers of C=N stretching bands in i.r. spectra of the dihydrotriazines were compared with those of (1). The results are shown in Table 1. Two isomeric *N*-methyl derivatives of (1) which showed different m.p.s, 191 and 210 °C, were isolated and assigned by Ritter and Anderson² as 2,2,4,6-tetraphenyl-3-methyl-2,3-dihydro-1,3,5-triazine (2a) and 2,2,4,6-tetraphenyl-5-methyl-2,5-dihydro-1,3,5-triazine (2b), respectively, on the basis of their u.v. absorption curves.

The i.r. spectrum of (2a) showed a C=N stretching band at 1 615 cm^{-1} and that of (2b) appeared at 1 645 cm^{-1} . This fact supported the assignment of the two C=N bands appearing in the i.r. spectrum of (1) to two tautomers, (1a and b), as described above. One of the two isomers of 2,2,4,6-tetraphenyl-2(5)-ethyldihydro-1,3,5-triazine (3) which showed a C=N band at 1 610 cm^{-1} was assigned to the 2,3-dihydro-form (3a), and the other with a band at 1 650 cm^{-1} was assigned to the 2,5-dihydro-form (3b). Compounds (4) and (5), each containing a bulky group on the ring nitrogen, gave a single isomer. They showed a C=N band at 1 655 cm^{-1} in their i.r. spectra and therefore they were suggested to be the 2,5-dihydro-forms (4b) and (5b). Although 2,4,6-triphenyldihydro-1,3,5-triazine (6), 2,4,6-triphenyl-2-methyldihydro-1,3,5-triazine (7), and 2,4,6-triphenyl-2-ethyldihydro-1,3,5-triazine (8) have been shown to exist in the 2,3-dihydro-form,^{3,4} the i.r. spectrum of each compound measured in chloroform solution exhibited two C=N bands indicating the presence of two isomers as shown in Table 1. In the solid state, however, both (6) and (8) showed no recognizable C=N band at ca. 1 680 cm^{-1} due to the (b) form. Dimethyl-2,4,6-triphenyldihydro-1,3,5-triazine (9) showed a C=N band at 1 605

Table 1. C=N Stretching bands in i.r. spectra for 2,3-dihydro- (a band) and 2,5-dihydro-1,3,5-triazines (b band)

Compound	a Band (cm^{-1})	b Band (cm^{-1})	Relative intensity a band:b band	Medium
(1)	1 612	1 685	3:1	KBr
(1)	1 620	1 690	4:3	CHCl_3
(2a)	1 615			KBr
(2b)		1 645		KBr
(3a)	1 610			KBr
(3b)		1 650		KBr
(4)		1 655		KBr
(5)		1 655		KBr
(6)	1 610			KBr
(6)	1 610	1 680	5:4	CHCl_3
(7)	1 610	1 680	3:1	KBr
(7)	1 610	1 683	3:1	CHCl_3
(8)	1 605			KBr
(8)	1 615	1 682	5:3	CHCl_3
(9)	1 605			KBr



	R ¹	R ²		R ¹	R ²
(1)	Ph	H	\rightleftharpoons	Ph	H
(2)	Ph	Me		Ph	Me
(3)	Ph	Et		Ph	Et
(4)				Ph	Bu^n
(5)				Ph	CH_2Ph
(6)	H	H	\rightleftharpoons	H	H
(7)	Me	H	\rightleftharpoons	Me	H
(8)	Et	H	\rightleftharpoons	Et	H
(9)	Me	Me			

cm^{-1} attributable to the 2,3-dihydro-form (a). From these facts it was reasonably concluded that (i) the 2,3-dihydro-form of dihydro-1,3,5-triazine ring shows a C=N stretching band in the vicinity of 1 610 cm^{-1} , whereas the 2,5-dihydro-form shows a C=N stretching band at 1 680—1 690 cm^{-1} in NH compounds and 1 645—1 655 cm^{-1} in *N*-substituted compounds; (ii) tri- and tetra-phenyldihydro-1,3,5-triazines containing a hydrogen on a ring nitrogen [(1), (6)—(8)] exist in a tautomeric equilibrium

Table 2. M.p., absorption maxima, and ϵ values of dihydrotriazines †

Compound	M.p. (°C) (lit.)	λ_{\max} (EtOH)/nm	($\epsilon \times 10^{-4}$)
(1)	192 (190–191) ¹	327 (0.14)	243 (2.5)
(2a)	196–197 (191) ²	323 (0.14)	249 (1.8)
(2b)	213–214 (210) ²		225 (3.7)
(3a)	222–223	320 (0.19)	251 (2.2)
(3b)	166–167		230 (2.5)
(4)	185–186		230 (1.0)
(5)	248–249		223 (2.7)
(6)	174–175 (175–177) ³	337 (0.19)	249 (2.2)
(7)	147 (143) ⁴	330 (0.19)	247 (1.9)
(8)	155 (155) ⁴	330 (0.16)	245 (2.0)
(9)	158–159 (156) ⁴	337 (0.24)	249 (2.1)

† Even for the known compounds no u.v. spectral data have been reported except for (2a and b)

between the 2,3-dihydro (a), and 2,5-dihydro (b) forms; (iii) the tautomeric equilibrium was shown to be biased towards the (a) form, which is considered to be more stable than the (b) form and the preferred tautomer, because of the presence of conjugated double bonds in the ring.

U.v. absorption curves for forms (a) and (b) showed significant differences between (2a) and (2b), or (3a) and (3b), as shown in Table 2, and for form (a), maxima indicating conjugation of the double bonds in the triazine ring. It was expected that each form (b) in (1) and (6)–(8) would show an absorption curve similar to that of (2b), (3b), (4), or (5); however, absorption curves for (1) and (6)–(8) looked like that of form (a), as in (2a) and (3a). Therefore u.v. spectroscopy does not make it clear that the compounds exist in the tautomeric equilibrium. The maximum due to form (b) in (1) and (6)–(8) appears at ca. 225 nm, and partly overlaps with the absorption band at ca. 245 nm for the corresponding form (a) which is preferred.

The existence of tautomers (1a) and (1b) was further confirmed by means of n.m.r. studies. The ¹H n.m.r. spectrum of (1) measured in [²H₂]dichloromethane at room temperature showed a broad signal at δ 6.15 attributable to the NH proton on the dihydrotriazine ring, and a signal for the phenyl protons at δ 6.7–8.5. With decreasing temperature, however, as shown in Table 3, the signal at δ 6.15 shifted to lower field (δ 6.37 at –40 °C) with another signal appearing (δ 7.99 at –40 °C) which was considered to be hidden in the signals of the phenyl protons at room temperature. Both signals at δ 6.37 and 7.99 exchanged with D₂O, indicating the existence of two kinds of NH proton in compound (1). In other solvents the two kinds of NH proton also appeared below room temperature as shown in Table 3. The signal intensity of the NH proton at higher field was larger than the other one in the three kinds of solvent used, and from the relative intensity of the two signals measured in [²H₆] acetone at –70 °C the relative concentration of the two kinds of NH proton was estimated to be ca. 2:1. The NH signal at higher field with stronger intensity was assigned to isomer (1a), and the lower field one was assigned to (1b). Support for the assignment is as follows: (i) the two double bonds adjacent to the NH group in the –N=C–NH–C=N– fragment of (1b) should bring a larger deshielding effect to the NH proton than

Table 3. ¹H N.m.r. chemical shifts (δ) of NH group in the tautomeric dihydrotriazines

Solvent	Compound	Temp. (°C)					
		+25	–20	–40	–50	–60	–70
CD ₂ Cl ₂	(1a)	6.15	6.28	6.37			
	(1b)		7.90	7.99			
(CD ₃) ₂ CO	(1a)				8.65		8.75
	(1b)	9.45			10.05		10.25
[² H ₈]THF	(1a)		8.32	8.42			
	(1b)		9.62	9.72			
CDCl ₃	(6a)	6.5			6.7		
	(6b)			7.77		7.8	
(CD ₃) ₂ CO	(6a)			8.87		8.9	
	(6b)			8.87		8.9	
CDCl ₃	(7a)	5.9		6.0			
	(8a) ^a	5.83			6.05		

† Measured with a JNM-FX 90 Q spectrometer.

in the –N=C–NH–C(Ph)₂– fragment in (1a); (ii) much larger solvation stability would be expected for the (b) than for the (a) form in which three phenyl groups on the two carbons bound to the NH group impede solvation of the NH proton; (iii) in the ¹H n.m.r. spectrum of the tautomeric isomers of 6-methyl-2,4-diphenyldihydropyrimidine,⁵ the 1,4-dihydro-form, which corresponds to (1b), shows a signal for the NH proton at lower field (δ 8.56) than that of 3,4-dihydro-form, which has a similar structure to (1a) (δ 8.06); (iv) in the ¹H n.m.r. spectra of *N*-alkyldihydrotriazines the signals for the NMe protons in (2a) and the methylene protons in the NCH₂R group in (3a) appeared at higher field than the corresponding signals in the (b) forms [NMe: (2a) δ 2.72, (2b) δ 2.85; NCH₂R: (3a) δ 3.25, (3b) δ 3.39].

¹H N.m.r. spectra of compounds (6)–(8), each of which was already shown to be a tautomeric mixture in CHCl₃ from their i.r. spectra, were also measured. Compound (6) showed a broad signal at δ 6.5 in CDCl₃ attributable to an NH proton, but no signal was found for the second NH proton expected of another tautomer even upon decreasing the temperature. For [²H₆]acetone, two signals for two kinds of NH proton appeared at the edge of the signals for phenyl protons below –40 °C (δ 7.8 and 8.9 at –60 °C), and for CDCl₃ the expected second signal probably due to form (b) was considered to be hidden in the phenyl protons signal. Compound (7) showed a broad signal for an NH proton at δ 5.9 in CDCl₃, probably due to (7a), but we failed to find two kinds of NH proton in CDCl₃ and also in [²H₈]THF even at –40 °C. The appearance of two kinds of methyl protons for the individual tautomers, (7a and b), was expected but only one signal (singlet) was shown at δ 1.899.* In compound (8) there was a signal for an NH proton at δ 5.83 in CDCl₃, probably for (8a), and another signal for (8b) was not found in the spectrum. The presence of two kinds of ethyl groups [Me: δ 1.01 (t) and 0.97 (t) (*J* 7.3 Hz); CH₂: δ 2.20 (q) and 2.17 (q) (*J* 7.3 Hz)], however, were shown. The intensity of the signal of methyl protons at δ 0.97 was bigger than that at δ 1.01, and the signal for the methylene protons at δ 2.20 was bigger than that at δ 2.17, in a ratio of ca. 5:3. The concentration ratio of the two kinds of ethyl group thus obtained in CDCl₃ was consistent with that observed in the i.r. spectrum: (8a): (8b) ca. 5:3 in CHCl₃. This in turn enables us to make a tentative assignment of the two ethyl groups for the individual tautomers (8a), δ 2.20 (CH₂) and 0.97 (Me); (8b), δ 2.17 (CH₂) and 1.01

* Measured with a JNM GX 270 spectrometer.

(Me). This assignment is supported by the following considerations; in (8b) two double bonds adjacent to the carbon at the 2-position which is bound to the ethyl group should have a stronger deshielding effect on the methylene protons in the ethyl group than in (8a). This corresponded to the fact that the methylene protons in the *N*-ethyl group in (3b) appeared at lower field than those of (3a) in their ^1H n.m.r. spectra.

From these findings it was confirmed that (6) and (8) exist in a tautomeric mixture of forms (a) and (b). Although confirmation for the presence of an equilibrium in (7) by using ^1H n.m.r. measurements failed, from the structural correlation between (7) and (1), (6), or (8) it was concluded that (7) also exists in a tautomeric mixture of (7a and b). It is uncertain, but no appreciable difference in chemical shifts between two methyl groups of (7a and b) seems to be the reason for our failure to find two kinds of methyl protons in ^1H n.m.r. spectrum of (7).

Experimental

I.r. spectra were recorded with a JASCO-A 302 spectrometer with a data processor, type DP-A 330. Different i.r. absorptions were measured for (1) and (6)–(8) in CHCl_3 by using the data processor. ^1H N.m.r. spectra were obtained with a JEM C-60HL or JNM-FX 90Q spectrometer with a JES-VT-3 variable-temperature controller, using tetramethylsilane as internal standard. U.v. spectra were obtained with a Shimadzu UV-200 spectrometer.

Materials.—Tri- or tetra-phenyldihydro-1,3,5-triazines (1) (2a), (2b), and (6)–(9) were known compounds and (3a), (3b), (4), and (5) were prepared from (1) by the method of Haines and Wagner⁶ for the preparation of *N*-alkylimidazoles. The yield of products was based on isolated materials. M.p.s, u.v. maxima, and ϵ values of (1)–(9) are summarized in Table 2.

2,2,4,6-Tetraphenyl-3-ethyl-2,3-dihydro-1,3,5-triazine (3a) and 2,2,4,6-Tetraphenyl-5-ethyl-2,5-dihydro-1,3,5-triazine (3b).—A mixture of 2,2,4,6-tetraphenyldihydro-1,3,5-triazine (1) (1 g, 2.6 mmol) and potassium (1 g, 26 mmol) in dioxane (40 ml) was heated for 4 h and then ethyl iodide (2.2 ml, 26 mmol) was added to the mixture. After the mixture was heated at 70 °C for 4 h, potassium iodide was removed by filtration, and the filtrate was evaporated *in vacuo*. The crude product was chromatographed on alumina with benzene as eluant to give (3a and b). Recrystallization of each product from ethanol gave columns of

(3a) and prisms of (3b): **compound (3a)**, 25% yield, δ_{H} (60 MHz; CDCl_3) 0.44 (3 H, t, J 7.5 Hz, Et), 3.25 (2 H, q, J 7.5 Hz, Et), and 6.85–8.40 (20 H, m, Ph) (Found: C, 84.0; H, 6.1; N, 9.95. $\text{C}_{29}\text{H}_{25}\text{N}_3$ requires C, 83.8; H, 6.1; N, 10.1%); **compound (3b)**, 34% yield; δ_{H} (60 MHz; CDCl_3) 0.18 (3 H, t, J 7.5 Hz, Et), 3.39 (2 H, q, J 7.5 Hz, Et), and 6.8–7.9 (20 H, m, Ph) (Found: C, 83.95; H, 6.1; N, 10.05%).

2,2,4,6-Tetraphenyl-5-*n*-butyl-2,5-dihydro-1,3,5-triazine (4).—This was prepared by the reaction of (1) with potassium and then *n*-butyl iodide in dioxane by the similar method to the preparation of (3a or b). The crude product was chromatographed on alumina to separate it from (1) with benzene as eluant. The product was recrystallized from benzene-ethanol to give prisms, 40% yield; δ_{H} (60 MHz; CCl_4) 0.4 (7 H, m, $\text{N-CH}_2\text{-Pr}^n$), 3.38 (2 H, t, J 7.2 Hz, N-CH_2), and 6.8–8.0 (20 H, m, Ph) (Found: C, 83.75; H, 6.6; N, 9.35. $\text{C}_{31}\text{H}_{29}\text{N}_3$ requires C, 83.9; H, 6.6; N, 9.45%).

2,2,4,6-Tetraphenyl-5-benzyl-2,5-dihydro-1,3,5-triazine (5).—This was prepared by the reaction of (1) with potassium and benzyl bromide in dioxane. After removal of potassium bromide by filtration from the mixture the filtrate was concentrated by evaporation to give prisms. The product was recrystallized from benzene to give (5) in 30% yield; δ_{H} (60 MHz; CDCl_3) 4.5 (2 H, s, N-CH_2), 5.8–6.9 (5 H, m, Ph), and 6.9–7.9 (20 H, m, Ph) (Found: C, 85.55; H, 5.7; N, 8.7. $\text{C}_{34}\text{H}_{27}\text{N}_3$ requires C, 85.5; H, 5.7; N, 8.8%).

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References

- 1 A. Lottermoser, *J. Prakt. Chem.*, 1896, **54** [2], 113.
- 2 J. J. Ritter and R. D. Anderson, *J. Org. Chem.*, 1959, **24**, 208.
- 3 H. L. Nyquist, *J. Org. Chem.*, 1966, **31**, 784.
- 4 R. H. Anker and A. H. Cook, *J. Chem. Soc.*, 1941, 323.
- 5 A. Weis and F. Frolow, *J. Chem. Soc., Chem. Commun.*, 1982, 89.
- 6 P. G. Haines and E. C. Wagner, *J. Am. Chem. Soc.*, 1949, **71**, 2793.

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