1,3,5-Triazines. Part VII.¹ The Ultraviolet, Infrared, and ¹H Nuclear Magnetic Resonance Spectra of Some Chloro-1,3,5-triazine Derivatives

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The structures of the arylamino- and p-dialkylaminophenyl-dichloro-1,3,5-triazine derivatives described previously ² are discussed in the light of their physical properties. The ultraviolet and ¹H nuclear magnetic resonance spectra of compounds of the latter class lead us to propose the triazinyl residue as a substituent group with a potentially variable electron-withdrawing power.

IN Part V² we described the reactions of a series of NN-dialkyl-anilines, -toluidines, and -xylidines with cyanuric chloride. Products of three types were isolated: colourless crystalline compounds (I); colourless low-melting solids or viscous oils (II); yellow crystalline compounds (III). One or more of these compounds were obtained from each reaction. The first two types were shown from their molecular weights and elemental analyses to be (N-alkyl-N-arylamino)-dichloro-1,3,5triazines(I) and di-(N-alkyl-N-arylamino)-chloro-1,3,5triazines (II). As previously,² we will term these "nitrogen-substituted" derivatives. The structures of compounds (III) were more complex. Their analyses are consistent with loss of hydrogen chloride from one molecule of arylamine and one of cyanuric chloride, suggesting that nuclear substitution had taken place in the former.

Infrared Spectra.—The product (I) from the reaction of NN-diethylaniline with cyanuric chloride has been unambiguously synthesised.³ In the region 650-900 cm.⁻¹ the pattern due to the aromatic carbon-hydrogen skeletal vibrations of the compounds of types (I) and (II) resembles a superposition of that of the starting amine and the triazine band at \sim 795 cm.⁻¹ (see Table 1). This similarity, which extends to all the "nitrogensubstituted " compounds reported here, has been noted

¹ Part VI, E. H. Amonoo-Neizer, R. C. Golesworthy, R. A. Shaw, and B. C. Smith, J. Chem. Soc., 1965, 5452.
 ² R. A. Shaw and P. Ward, J. Chem. Soc., 1965, 5446.
 ³ R. C. Golesworthy, R. A. Shaw, and B. C. Smith, J. Chem.

Soc., 1962, 1507.

by other workers.⁴ The dichloro-derivatives (I) differed from the monochloro-compounds (II) in showing a very strong band at 840 cm.⁻¹, due to a complex C-Cl stretching mode involving part of the triazine ring.⁵ This band is diagnostic of dichloro-monosubstituted-1,3,5-triazines and of cyanuric chloride.



A decision on the structure of the "carbon-substituted " derivatives (III) is more complex, as the position of substitution in the benzene ring by the triazine group must be ascertained. Whilst consideration of the reaction of phenoxides,⁶ acting as ambident anionic nucleophiles, favours the ortho-position, the work of McKusick et al. on the more closely analogous reactions of N-methyl- and NN-dimethyl-aniline with tetracyanoethylene and tricyanovinyl chloride shows, as

⁴ P. Fontana, M. Amorosa, and L. Alfieri, Pubbl. univ. cattolica S. Cuore, Ann. fac. agrari., 1960, 77, 115 (Chem. Abs., ⁵ W. A. Heckle, H. A. Orey, and J. M. Talburt, Spectrochim.

Acta, 1961, 17, 600.

⁶ Cf. R. Gompper, Angew. Chem., Internat. Ed., 1964, 3, 525.

confirmed by degradation, that reaction takes place in these systems at the para-position.⁷

Synthesis by an unambiguous route of (III; $R^1 =$ Et, $R^2 = R^3 = H$),³ and comparison of infrared spectra, m. p., and mixed m. p., shows that substitution has taken place para to the diethylamino group. The infrared spectra of the "carbon-substituted" compounds (III) derived from NN-dialkylanilines show in the region 1650-2000 cm.⁻¹ absorption patterns which are closely similar to each other as well as to those of 4-nitro-NN-diethylaniline and p-diethylaminobenzaldehyde. Bellamy⁸ states that this region affords the best and most selective method for identifying the position of substitution. This evidence suggests that the triazinyl group is para to the amino group in all compounds reported here.

Recently a detailed correlation of data derived from the aromatic ¹H n.m.r. spectra of para-disubstituted



benzenes (S-values) and the electron-withdrawing and -donating powers of substituents on the benzene ring was made.¹⁰ The following S_0 values have been obtained:

TABLE 1

Infrared spectra (650-900 cm.⁻¹) of some arylamines and their N-(dichloro-1,3,5-triazine) derivatives

Substituent *	Arylamine					Triazine derivative							
NN-Di-Me	695 695		767 767		,	697 690 †	771		798 791	805(w)		838	
NN-Di-Et	$\begin{array}{c} 695 \\ 695 \end{array}$		755 755		798 798	695 695 †	760(d) 750(m)		795 796	805(w)		840	
NN-Di-Pr ⁿ	698 700		751		852	697	742	772	795			840	849
NN-Di-Bu ⁿ	700 695		752 748		860	702 695	742	781	793 795			$\frac{840}{840}$	850
NN-Di-Et-2-Me	$715 \\ 695$		$750 \\ 765$	790	840(m)	718 695	758	700	$795 \\ 795$	806		840 840	
NN-Di-Et-4-Me	000		700	812	010(11)	055		190	795	823		840	
<i>NN</i> -Di-E t-2 ,3-di-Me <i>NN</i> -Di-E t-2 ,5-di-Me		730		$\begin{array}{c} 780 \\ 803 \end{array}$	812	720		780	$\begin{array}{c} 795 \\ 792 \end{array}$	801	815	$\frac{840}{840}$	
NN-Di-Et-2,6-di-Me	605	795	759	770		60F	741	770	795	001	010	841	
ми-Di-Сп ₂ РП	099	135	103			099	/41	100	195			840	

w = Weak, m = multiplet, d = doublet.

* All amino groups are in the 1-position. † Di-(N-alkyl-N-arylamino)-chloro-1,3,5-triazines (II).

¹H Nuclear Magnetic Resonance Spectra.—Similar conclusions may be drawn from the aromatic ¹H n.m.r. spectra of compounds (III). The aniline derivatives (IV) all show a pair of doublets characteristic⁹ of an $A_{2}B_{2}$ type of spectrum in the aromatic region. The chemical shifts and spin-spin coupling constants are shown in Table 2. The pair of protons ortho to the dialkylamino group are observed as a doublet at higher field than those ortho to the triazine moiety, because of the greater shielding experienced by the former protons. The toluidine derivative (V) gives an ABC type of spectrum which can only be rationalised with the triazine group's being ortho to the methyl and para to the diethylamino group. The spectrum of the xylidine derivative (VI) shows a single absorption in this region due to two equivalent aromatic protons. This, together with the chemical shift, shows that substitution must again have occurred para to the diethylamino group.

7 B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman, and H. F. Mower, J. Amer. Chem. Soc., 1958, 80, 2806; C. L. Dickinson, D. W. Wiley, and B. C. McKusick, *ibid.*, 1960, 82, 6132.

NO₂, -99; COCl, -86; SO₂Cl, -83; CO₂Me, -81; COMe, -68; CHO, -60.10 By a similar calculation, we derive the value of -78 for $C_3N_3Cl_2$. This value gives a fair indication of the order of electron-withdrawing power of the dichlorotriazinyl group, and is confirmed by the results obtained by ultraviolet spectroscopy presented below.

Horrobin¹¹ showed from basicity measurements that the dichlorotriazinyl group is strongly electron-withdrawing, but less so than the toluene-p-sulphonyl group.

Ultraviolet Spectra.-The spectra of compounds of types (I), (II), and (III) will be discussed under the separate headings of (a) "nitrogen-substituted" derivatives, (I) and (II), and (b) "para-carbon-substituted" derivatives, (III).

(a) These compounds all possess the general structures shown earlier and give the spectra detailed in the Figure

⁸ J. L. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 1960.
⁹ R. L. Batdorf, Ph.D. Thesis, University of Minnesota, 1955.
¹⁰ G. W. Smith, J. Mol. Spectroscopy, 1964, 12, 146.
¹¹ S. Horrobin, J. Chem. Soc., 1963, 4130.

and Table 3, from which it can be seen that there is a maximum at about 244 m μ and another at a much shorter wavelength ($\sim 204 \text{ m}\mu$). This latter peak is at the beginning of the solvent cut-off, and hence little reliance may be placed on its values.

TABLE 2

Aromatic ¹H n.m.r. spectra of arylamine derivatives of type (III)

			J_{AB}	Integr- ated
Substituent *	$\tau_{\mathbf{A}}$	$\tau_{\mathbf{B}}$	(c./sec.)	ratio
NN-di-Et-4-C ₃ N ₃ Cl ₂	1.69	3.31	10.5	2:2
NN -di-Pr ⁿ -4- $\mathring{C}_{3}N_{3}Cl_{2}$	1.62	3.26	11.0	2:2
NN-di-Pr ⁱ -4-C ₃ N ₃ Cl ₂	1.62	3.11	12.0	2:2
NN-di-Bu ⁿ -4-C ₃ N ₃ Cl ₂	1.64	3.27	9·0	2:2
NN-di-Et-3-Me-4-C ₃ N ₃ Cl ₂	1.63	3 ∙ 4 0 †	7.0	1:2
NN-di-Et-3,5-di-Me-4-C ₃ N ₃ Cl ₂		3.43		

* All amino groups are in 1-position. † Absorption due to B and C protons.

Wepster and his co-workers 12 showed that, in the series NN-dimethyl-aniline, -o-toluidine, and -2,6-xylidine, the extinction coefficients decrease at the absorption maximum owing to steric interference with mesomerism. We have confirmed these results for the NN-diethyl derivatives. There is no similar trend in the triazinyl compounds, the extinction coefficients remaining fairly constant (Table 3).

TABLE 3

Ultraviolet spectra of "nitrogen-substituted " derivatives of types (I) and (II)

			21	· · ·	()	
	\mathbf{R}^{1}	R1′	\mathbb{R}^2	\mathbf{R}^{3}	λ _{max.} (mμ)	10 ⁻³ ε
(I)	Me		\mathbf{H}	н	244	9.8
• •	Et		н	н	245 *	15.3 *
[(CH ₂] ₄ Cl		н	н	246	15.5
-	Pr ⁿ		н	н	242	19.3
	Bu ⁿ		н	н	246	12.8
	Et		2-Me	\mathbf{H}	243 †	20.8 +
	\mathbf{Et}		3-Me	н	245	13.8
	Et		4-Me	н	245	17.2
	Et		2-Me	3-Me	241	17.3
	\mathbf{Et}		2 -Me	5-Me	243	17.8
	Et		2 -Me	6-Me	243 ‡	17·8 ‡
	Et		3-Me	5-Me	244.5	15.4
(II)	\mathbf{Me}	Me			246	22.5
	${ m Me}$	\mathbf{Et}			246	$25 \cdot 8$
	Et	Et			246	$29 \cdot 9$
	$[CH_2]_4Cl$	$[CH_2]_4Cl$			249	31.2
,	• For NN	<i>I</i> -diethylani	line, 250) mµ,	17.8×10^{-3} .	† For
NI	V-diethyl-o	-toluidine,	249 mµ,	$5.8 \times$	10-3. <u>t</u> For	NN-di-

ethyl-2,6-xylidine, 258 mµ, 1.3×10^{-3} .

A probable explanation of this contrasting behaviour is that, whilst the band under examination in the NN-dialkyl derivatives is the aromatic K-band.¹² this is not the case with the triazinyl derivatives, in which the lone-pair of electrons on the exocyclic nitrogen atom is conjugated not with the aromatic nucleus but with the more strongly electron-withdrawing triazine group. Thus, the band observed is due to the nitrogentriazine conjugation superimposed upon the virtually unperturbed aromatic absorption. Confirmation of

¹² J. Burgess, M. A. Hoefnagel, P. E. Verkade, H. Visser, and B. M. Wepster, Rec. Trav. chim., 1958, 77, 419.

this hypothesis comes from Koopman's 13 observation that 2,4-dichloro-6-dimethylamino-1,3,5-triazine has $\lambda_{\text{max.}}$ (241 mµ) and $\varepsilon_{\text{max.}}$ (20,400) similar to those of the amino-derivatives described above.

When more than one chlorine atom is replaced in cyanuric chloride the influence of the auxochromes upon the extinction coefficient is approximately additive.¹³ Several thio- and amino-derivatives obey this rule, and it has been confirmed by us for a number of others (see Table 3). Koopman was unable to explain this, but we suggest that it is due to the triazine acting as an insulator of both the strongly polar and the metaphenylene types.

(b) Koopman¹³ studied the ultraviolet spectra of a series of 2-(para-substituted phenyl)-4,6-dichloro-1,3,5triazines, and some of his results are shown with those



A, 2-(N-Alkyl-N-arylamino)-4,6-dichloro-1,3,5-triazine B, 2,4-Di-(N-alkyl-N-arylamino)-6-chloro-1,3,5-triazine

C, 2,4-Dichloro-6-(4-dialkylaminophenyl)-1,3,5-triazine

from the present study in Table 4 (see Figure for general shape of curves).

The wavelength of maximum absorption and the extinction coefficient at the maximum increases with

		Tabl	Е4	
Ult	raviolet s	pectra of "	carbon-subst	ituted "
		derivativ	es (III)	
Y *	\mathbb{R}^2	R ³	$\lambda_{max.}$ (m μ)	10 ⁻³ ε
NEt ₂	н	н	403	51.5
NPr ⁿ ,	н	н	407	45.5
NPr ⁱ ,	н	H	408	49.3
NBu ⁿ ,	н	н	405	54.2
NEt,	3-Me	н	403	50.3
NEt,	3-Me	5-Me	392	49.5
SMe	н	\mathbf{H}	347	30.5 (ref. 13)
OMe	н	\mathbf{H}	332	30.8 (ref. 13)
н	H	н	276	21.3 (ref. 13)
	C			

Substituent Y is always in the 1-position.

increasing electron-donating power of the substituent. Koopman considers this absorption to be due to changes in the electronic ground state of the triazine. However, from the work of Doub and Vandenbelt on mono- and para-di-substituted benzene derivatives,¹⁴ a different

 ¹³ H. Koopman, Rec. Trav. chim., 1961, **80**, 158.
 ¹⁴ L. Doub and J. M. Vandenbelt, J. Amer. Chem. Soc., 1947, **69**, 2714.

picture emerges. These authors showed that substituents may be divided into two classes, electron-donating and electron-accepting. With one substituent from each category in the *para*-position, the K-band of benzene moves to longer wavelength and has a greater extinction coefficient than would be expected from a purely additive effect. This has a semi-quantitative value, as replacement of the electron-withdrawing group by a more strongly electron-withdrawing group moves the maximum to longer wavelength. Similarly, replacement of an electron-donating group by a more strongly electron-donating group also moves the maximum to longer wavelengths.

By considering compounds of type (III) as benzene derivatives with a strongly electron-donating group (the dialkylamino), and a strongly electron-withdrawing group (the 2,4-dichloro-1,3,5-triazinyl) in *para*-positions to each other, it seems most likely that the band under discussion is the K-band of benzene. It may also be deduced that, as the maximum in the triazinyl compounds occurs near 400 m μ , this substituent has an electron-withdrawing power of the order of that of the nitro group.

This observation leads us to propose the dichloro-1,3,5-triazinyl group as a useful substituent group with a potentially variable electron-withdrawing power. This is because the changes, produced by varying the triazine moiety, are purely electronic in origin. The steric and electrostatic differences usually attendant upon changing a substituent group are constant for this series. As described below, these triazine moieties are readily interconvertible *in situ*. For example, the

TABLE 5

The	ιH	n.m.r	. and	ultraviol	et spec	tra, an	d the	pK_a'
values,	of	some	<i>p</i> -diet	hylamine	opheny	ltriazi	ne der	ivatives

Compound	S,	λ _{max.} (mμ)	$rac{\epsilon_{max.}}{ imes 10^{-3}}$	p <i>K</i> a' in PhNO ₂
2,4-Dichloro-6-(4-diethylamino- phenyl)-1,3,5-triazine 2-Chloro-4-dimethylamino-6-(4-	-78	403	51.5	-2.8
diethylaminophenyl)-1,3,5-tri- azine	-71	348	44 ·5	-0.8
ethylaminophenyl)-1,3,5-tri- azine	-63	334	40 ·0	3.4

chlorine atoms can be easily replaced in a stepwise fashion by, *e.g.*, dimethylamino residues, giving a group which, on replacement of one chlorine atom, is slightly less electron-withdrawing than the nitrogroup, and on replacement of both chlorine atoms is of

¹⁵ D. Feakins, W. A. Last, and R. A. Shaw, J. Chem. Soc., 1964, 2387.

the same order as the aldehyde group. The ¹H n.m.r. and ultraviolet spectroscopic data, and $pK_a'^{15}$ values in nitrobenzene (Table 5) illustrate this comparison.¹⁶ The absorption spectra of all three compounds in acid solution are similar, and the now colourless solutions have maxima at much shorter wavelengths than the free bases, showing that the first proton becomes attached in all three cases to the nitrogen atom of the NN-diethylamino group.

EXPERIMENTAL

Melting points were observed in a Reichert-Kofler micro-heating stage fitted with a polarising microscope. The preparations of the triazine derivatives (except the dimethylamino-compounds) were described previously.² Acetone was of AnalaR grade, and the light petroleum had b. p. $60-80^{\circ}$.

2-Chloro-4-dimethylamino-6-(4-diethylaminophenyl)-1,3,5triazine.— 2,4-Dichloro-6-(4-diethylaminophenyl)-1,3,5-triazine (300 mg.) dissolved in acetone (50 ml.) was poured slowly with vigorous stirring into water (100 ml.) at icebath temperature. Dimethylamine (0.6 g.) in acetone (20 ml.) was added dropwise during 3 min. The mixture was stirred at ice-bath temperature (1 hr.), poured into water (200 ml.), and filtered. The residue was dried in a dessicator at room temperature to give the *product* (277 mg., 91%), m. p. 118—118.5° (after two recrystallisations from light petroleum) (Found: C, 59.0; H, 6.7; Cl, 11.5; N, 22.9 C₁₅H₂₀ClN₅ requires C, 58.9; H, 6.6; Cl, 11.6; N, 22.9%).

2,4-Bisdimethylamino-6-(4-diethylaminophenyl)-1,3,5-triazine.— 2,4-Dichloro-6-(4-diethylaminophenyl)-1,3,5-triazine (300 mg.) dissolved in acetone (50 ml.) was poured with vigorous stirring into water (100 ml.) at ice-bath temperature. Dimethylamine (4.0 g.) in acetone was added. The cooling-bath was removed and the reaction mixture gently heated to its boiling point, refluxed ($\frac{3}{4}$ hr.), cooled, and poured into water (200 ml.). Filtration and drying in a dessicator gave the *product* (283 mg., 89%), m. p. 151-153° (after two recrystallisations from light petroleum) (Found: C, 65.3; H, 8.2; N, 26.6. C₁₇H₂₆N₆ requires C, 64.9; H, 8.3; N, 26.7%).

Spectra.—Infrared spectra (KBr discs) were measured using an SP 100 recording spectrophotometer operating as a double-beam instrument. ¹H N.m.r. spectra were obtained for 20% w/v solutions in deuteriochloroform with a Varian Associates A60 spectrophotometer equipped with a 60 Mc/sec. radiofrequency source. Ultraviolet spectra were determined with a Unicam SP 700 recording spectrophotometer in the region 200—833 mµ; analytically pure samples dissolved in ethanol (96%) were contained in 1 cm. matched silica cells, and Beer's law was obeyed in the many cases tested.

[6/990 Received, August 4th, 1966]

¹⁶ D. Feakins, W. A. Last, S. N. Nabi, and R. A. Shaw, unpublished results.