

**810. The Structure of Two *N*-oxides of 3,5,6-Triphenyl-1,2,4-Triazine: Evidence from Dipole Moments.**

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*N*-Oxidation of 3,5,6-triphenyl-1,2,4-triazine gives two *N*-oxides to which structures have been assigned, as *N*-1 and *N*-2 oxides, on the basis of measurements and deductions from related *N*-heterocycles.

DURING a general study of 1,2,4-triazines, it was found that *N*-oxidation of 3,5,6-triphenyl-1,2,4-triazine yielded a mixture of two isomers. Strong evidence for the site of *N*-oxidation in these isomers is provided by a study of the dipole moments, measured in benzene, of the compounds listed in Table 1.

TABLE 1.

Polarisation data for benzene solutions at 25°.

Compound	$10^3\alpha$	$10^2\nu$	$P_{2\infty}$ (c.c.)	$\mu$ (D)
Pyridazine .....	23,303	9	349.9	4.14
2,5-Dimethylpyrazine-1-oxide .....	2,854	21	61.7	1.74
4,6-Dimethylpyrimidine .....	7,024	—5	144.0	2.65
4,6-Dimethylpyrimidine-1-oxide .....	13,253	23	304.2	3.86
3,5,6-Triphenyl-1,2,4-triazine .....	3,789	40	197.2	3.10
3- <i>p</i> -Chlorophenyl-5,6-diphenyl-1,2,4-triazine .....	5,335	48	313.3	3.91
3- <i>p</i> -Bromophenyl-5,6-diphenyl-1,2,4-triazine .....	4,802	46	317.0	3.94
3,5,6-Triphenyl-1,2,4-triazine- <i>N</i> -oxide				
Compound 1 .....	5,013	48	277.0	3.68
Compound 2 .....	6,112	55	339.9	4.08

## 4210 Atkinson, Ibbitson, Rice, and Sandall: The Structure of

Because the pyridine ring is  $\pi$ -electron-deficient compared to the benzene ring, it is to be expected that corresponding substituent-group moments will differ. From the moments of pyridine (2.22D),<sup>1</sup> 4-methylpyridine (2.61D),<sup>1</sup> and 4-chloropyridine (0.78D),<sup>1</sup> the moments of the methyl and chloro groups are calculated to be 0.39 and 1.44D, respectively, whereas the moments of toluene and chlorobenzene are 0.37 and 1.58D.

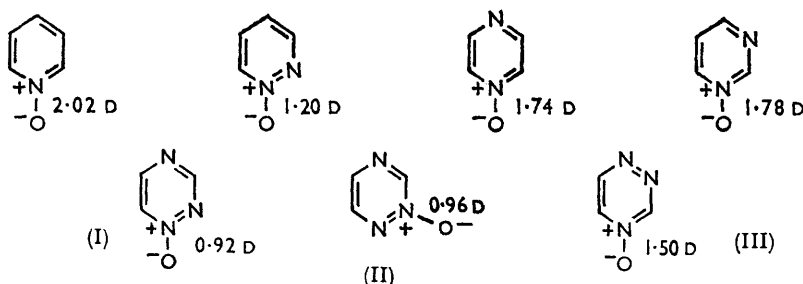
Using these group moments and the moments of 3-methylpyridazine (recalculated as 4.15D from Smith's formula)<sup>2</sup> and 3-methyl-6-chloropyridazine (4.51D),<sup>2</sup> two values of the pyridazine-ring moment (4.13, 4.12D), each bisecting the two nitrogen atoms were calculated vectorially. The excellent agreement with the observed value for pyridazine (4.14D) implies that interactions between the nitrogen atoms and the *ortho*-chloro- and *ortho*-methyl substituents do not affect the moment of pyridazine.

From the moments of pyridazine (4.14D) and pyridazine-1-oxide (5.21D),<sup>3</sup> the N-O group moment was computed vectorially, and found to be 1.20D. Similarly, using the moments of 3-methylpyridazine-1-oxide (5.23D),<sup>2</sup> 3-methylpyridazine-2-oxide (5.23D),<sup>2</sup> and 3-methyl-6-chloropyridazine-2-oxide (5.29D),<sup>2</sup> N-O group moments were calculated to be 1.16, 1.26, and 1.18D, respectively. Thus the presence of adjacent methyl and chloro groups does not affect greatly the N-O group moments, and it was considered reasonable to assume a mean value of 1.20D for the N-O group moment when the oxygen atom is bonded to a nitrogen atom adjacent to a second nitrogen atom.

Values of the N-O group moments in pyridine-1-oxide, pyrazine-1-oxide, and pyrimidine-1-oxide are also necessary to solve the present problem. From the moments of pyridine (2.22D) and pyridine-1-oxide (4.24D),<sup>1</sup> the N-O group moment was calculated to be 2.02D. Since 2,5-dimethylpyrazine is non-polar, the N-O group moment in 2,5-dimethylpyrazine-1-oxide was taken to be the observed moment of this compound (1.74D). The N-O group moment in 4,6-dimethylpyrimidine-1-oxide was calculated vectorially to be 1.78D, assuming the moment of 4,6-dimethylpyrimidine (2.65D) acting at 60° to the direction of the N-O bond, and the moment of 4,6-dimethylpyrimidine-1-oxide (3.86D).

Essential N-O bond moments are illustrated in the Figure, those of 1,2,4-triazine-N-oxides being calculated additively from those of the diazines.

The angle,  $\alpha$ , which the moment of 3,5,6-triphenyl-1,2,4-triazine (3.10D) makes with the  $N_1-N_4$  axis was calculated by Marsden and Sutton's method<sup>4</sup> from the moments of



Calculation of the N-O group moments in the 1,2,4-triazine-N-oxides, from those of the diazines.

$$\begin{aligned} \text{(i)} \quad \mu_{\text{NO}} &= 0.92 = 1.20 - (2.02 - 1.74) \\ \text{(ii)} \quad \mu_{\text{NO}} &= 0.96 = 1.20 - (2.02 - 1.78) \\ \text{(iii)} \quad \mu_{\text{NO}} &= 1.50 = 1.78 - (2.02 - 1.74) \end{aligned}$$

3-*p*-chlorophenyl-5,6-diphenyl-1,2,4-triazine (3.91D) and chlorobenzene (1.58D) ( $\alpha = 48^\circ 57'$ ). Using the moments of 3-*p*-bromophenyl-5,6-diphenyl-1,2,4-triazine (3.94D) and bromobenzene (1.56D), the value of  $\alpha(51^\circ 6')$  was found to be in good agreement. Taking a

<sup>1</sup> Katritzky, Randall, and Sutton, *J.*, 1957, 1769.

<sup>2</sup> Kano, Ogato, Watanabe, and Ishizuka, *Chem. Pharm. Bull.*, 1961, **9**, 1017.

<sup>3</sup> Watanabe, Ogata, and Kano, *Chem. Pharm. Bull.*, 1963, **11**, 39.

<sup>4</sup> Marsden and Sutton, *J.*, 1936, 599.

mean value of  $50^\circ$ , and using the N-O group moments deduced for the triazines (Figure), the moments of the 1-,2-,4-oxide isomers of 3,5,6-triphenyl-1,2,4-triazine were calculated to be 3.76, 4.05, and 2.43D, respectively. Comparing these values with those observed for the two N-oxides (compound 1, m. p.  $207^\circ$ ,  $\mu = 3.68\text{D}$ ; compound 2, m. p.  $194^\circ$ ,  $\mu = 4.08\text{D}$ ) leads to the conclusion that N-oxidation in compound 1 occurs at the  $N_1$  nitrogen atom, and in compound 2 at the  $N_2$  nitrogen atom.

We hope to discuss the relationship of the site of N-oxidation in this series with that of quaternisation.<sup>5</sup>

#### EXPERIMENTAL

*Materials.*—Benzene and cyclohexane, dried over sodium wire, were distilled, and the fractions b. p.  $80.1/760$  mm. and  $80.8^\circ/760$  mm. collected. "Spectrosol" carbon tetrachloride was distilled, fraction b. p.  $76.8^\circ/760$  mm. being stored over phosphorus pentoxide for 24 hr. before use. Pyridazine picrate, m. p.  $168-169^\circ$ , was recrystallised from alcohol and cleaved in alkaline solution. The pyridazine was distilled, fraction b. p.  $207-208^\circ$  being collected. 2,5-Dimethylpyrazine-1-oxide, m. p.  $107-108^\circ$ , prepared from commercial 2,5-dimethylpyrazine by Klein and Berkowitz's<sup>6</sup> method was repeatedly vacuum-sublimed. The dipole moment was determined immediately after purification. Commercial 4,6-dimethylpyrimidine was distilled, the fraction b. p.  $154-155^\circ/760$  mm. being collected. 4,6-Dimethylpyrimidine-1-oxide, m. p.  $112-113^\circ$ , prepared from 4,6-dimethylpyrimidine by Hunt, McOmie, and Sayer's<sup>7</sup> method, was recrystallised from petroleum ether (b. p.  $60-80^\circ$ ).

3,5,6-Triphenyl-1,2,4-triazine-N-oxides (with H. D. COSSEY).—The triazine (5 g.) was heated under reflux at  $80^\circ$  with acetic acid (75 ml.) and 30% hydrogen peroxide (25 ml.) for  $2\frac{1}{2}$  hr. The pale yellow needles (2.1 g.), m. p.  $119-204^\circ$ , which separated were collected cold and recrystallised from ethyl acetate to give pale yellow needles of a mono-N-oxide (1.75 g., 33%), m. p.  $207-208^\circ$  (Found: C, 77.2; H, 4.6; N, 12.9. Calc. for  $\text{C}_{21}\text{H}_{15}\text{N}_3\text{O}$ : C, 77.5; H, 4.65; N, 13.0%). The mixture was poured into water, and the yellow oily solid (1.25 g.) which separated was washed with water and dried. Recrystallisation from ethanol gave yellow needles of a mono-N-oxide (0.41 g., 8%), m. p.  $192-194^\circ$  (Found: C, 77.1; H, 4.4; N, 12.9. Calc. for  $\text{C}_{21}\text{H}_{15}\text{N}_3\text{O}$  as above.)

The remaining compounds were prepared as described previously.<sup>8</sup>

*Dipole Moments.*—Dielectric constants and refractive indices of solutions of graded concentrations in benzene were determined for each compound. All measurements were made at  $25^\circ$ .

Dielectric constants, accurate to  $\pm 0.0001$ , were measured with a heterodyne-beat dipolemeter (type DM 01, manufactured by Wissenschaftlich-Technische Werkstätten G.m.b.H.) with internal thermostatic control. The dielectric cell, type DFL1, of 20 ml. capacity, was provided with gold-coated interior plates and thermostat. The linear condenser was calibrated from measurements with benzene ( $\epsilon = 2.2725$ ), cyclohexane ( $\epsilon = 2.0139$ ), and carbon tetrachloride ( $\epsilon = 2.2274$ ).

Refractive indices were measured with an Abbé refractometer of high accuracy.

The results are summarised in Table 2, where the symbols have their usual significance.

The molar orientation polarisation at infinite dilution,  $P_{2\infty}$ , of each compound was calculated from the equation:

$$P_{2\infty} = 3M_2 v_1 \{ \alpha / (\epsilon_1 + 2)^2 - \nu / (n_1^2 + 2)^2 \}$$

in which  $M_2$  = molecular weight of solute,  $v_1$ ,  $\epsilon_1$ , and  $n_1$  are the specific volume, dielectric constant, and refractive index of the solvent, respectively, at  $25.0^\circ$ ,  $\alpha = (d\epsilon/dw)_{w=0}$ ,  $\nu = (dn^2/dw)_{w=0}$ ,  $\alpha$  and  $\nu$  were determined from the equations  $\alpha = \Sigma(\epsilon - \epsilon_1) / \Sigma w$  and  $\nu = \Sigma(n^2 - n_1^2) / \Sigma w$ . Dipole moments ( $\mu$ ) were calculated from the equation:

$$\mu = 0.012812 (P_{2\infty} \times T)^{\frac{1}{2}}$$

<sup>5</sup> Atkinson and Cossey, *J.*, 1962, 1628.

<sup>6</sup> Klein and Berkowitz, *J. Amer. Chem. Soc.*, 1959, **81**, 5160.

<sup>7</sup> Hunt, McOmie, and Sayer, *J.*, 1959, 527.

<sup>8</sup> Atkinson and Cossey, *J.*, 1962, 1805.

TABLE 2.

100w	$\epsilon$	$n_D$	100w	$\epsilon$	$n_D$	100w	$\epsilon$	$n_D$
Pyridazine			4,6-Dimethylpyrimidine-1-oxide			3- <i>p</i> -Bromophenyl-5,6-diphenyl-1,2,4-triazine		
0-0000	2-2720	1-49800	0-0000	2-2718	1-49805	0-0000	2-2721	1-49802
0-2138	2-3230	—	0-1402	2-2903	—	0-0723	2-2756	—
0-4082	2-3675	—	0-3346	2-3163	—	0-1316	2-2784	—
0-5348	—	1-49816	0-5729	2-3476	1-49849	0-2018	2-2818	1-49833
0-8017	2-4579	1-49823	0-7268	2-3682	1-49861	0-2630	2-2847	1-49842
0-9932	2-5025	1-49829	0-9469	2-3972	1-49877	0-3536	2-2891	1-49856
1-3877	2-5957	1-49839	1-1199	2-4203	1-49891	0-4355	2-2930	1-49868
2,5-Dimethylpyrazine-1-oxide			3,5,6-Triphenyl-1,2,4-triazine			3,5,6-Triphenyl-1,2,4-triazine- <i>N</i> -oxide (Compound 1)		
0-0000	2-2723	1-49805	0-0000	2-2728	1-49802	0-0000	2-2720	1-49803
0-2211	2-2787	—	0-1336	2-2778	—	0-0716	2-2758	—
0-3750	2-2831	—	0-2023	2-2805	1-49829	0-1198	2-2784	—
0-5775	2-2887	1-49845	0-2611	2-2827	1-49836	0-1367	2-2790	1-49825
0-7578	2-2937	1-49858	0-3337	2-2855	1-49846	0-1828	2-2813	1-49833
0-8305	2-2961	1-49863	0-4179	2-2886	1-49857	0-2268	2-2833	1-49840
0-9170	2-2985	1-49870				0-2737	2-2861	1-49847
4,6-Dimethylpyrimidine			3- <i>p</i> -Chlorophenyl-5,6-diphenyl-1,2,4-triazine			(Compound 2)		
0-0000	2-2720	1-49803	0-00000	2-2732	1-49807	0-00000	2-2724	1-49803
0-2487	2-2891	—	0-02269	2-2744	—	0-03442	2-2747	—
0-6032	2-3144	—	0-04583	2-2756	—	0-06423	2-2764	—
0-6298	2-3159	1-49792	0-06872	2-2769	1-49818	0-09716	2-2783	1-49821
0-8589	2-3325	1-49789	0-09110	—	1-49822	0-1276	2-2801	1-49827
1-1190	2-3510	1-49784	0-11436	2-2793	1-49825	0-1564	2-2818	1-49832
1-5319	2-3797	1-49777	0-13642	2-2805	1-49829	0-2270	2-2863	1-49844

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