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# s-TRIAZINES—VII

## SYNTHESIS OF DIHALOGENO-HETEROARYL-s-TRIAZINES. REACTION OF 2,4,6-TRICHLORO-s-TRIAZINE WITH N-HETEROAROMATIC RINGS

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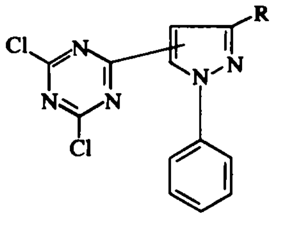
**Abstract**—2,4-Dichloro-6-(1-phenylpyrazol-5-yl)-s-triazine **1** and its 3-methyl analogue **2** have been prepared by reacting the lithiated derivatives of 1-phenylpyrazole and 3-methyl-1-phenylpyrazole respectively with 2,4,6-trichloro-s-triazine. The reaction fails with 1-methylimidazole, thiazole, benzothiazole and pyridine. The formation of an unstable quaternary salt is indicated in such cases. The isolation of 2,4-dimethoxy-6-(1-methyl-3-imidazolium)-s-triazine chloride (**6**, X=$OCH_3$) is reported. The synthesis and stability of 2,4-dichloro-6-(2-pyridyl)-s-triazine (**12**) are also described.

In the earlier paper[1] we reported the synthesis of dichloroheteroaryl-s-triazines by reacting 2,4,6-trichloro-s-triazine (cyanuric chloride) with a metalated derivative of pyrrole, thiophene or furan. Since selective lithiation of various aromatic and heteroaromatic compounds is now feasible, the above reaction can be extended to other heteroaromatic systems. The course of such reactions would be determined by the stability of the lithiated derivative and basicity of the nitrogen contained in a N-heteroaromatic ring. There are two papers[2,3] which report quaternary salt formation of cyanuric chloride with the pyridine nitrogen and also an unlikely nucleophilic attack by the 2- and 4-position of the pyridine nucleus. Thus it would be interesting to see whether a nucleophilic attack by the carbanion of the organo-metallic reagent would be favoured over the quaternisation particularly at low temperatures under the reaction conditions. Cyanuric chloride is known to react with various ambident nucleophiles[4] to give both N and C substituted products. Its reaction with various tertiary amines to give s-triazines substituted by secondary amino groups has been reported.[5] It has been postulated that during such reactions a quaternary ammonium salt is formed initially, which by elimination of alkyl halide leads to the product.

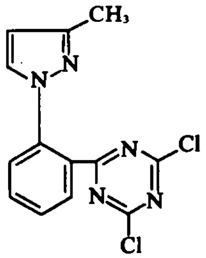
In the present paper, we report on the reaction of cyanuric chloride with the metalated derivatives of several heteroaromatic systems. The reaction, although successful with the lithiated derivatives of 1-phenylpyrazole, and 3-methyl-1-phenylpyrazole, failed to produce any isolable products with metalated derivatives of 1-methylimidazole, thiazole, benzothiazole, and pyridine. The reaction of 1-methylimidazole and pyridine with cyanuric chloride indicated formation of an unstable quaternary salt in each case. The isolation of such quaternary salt from the reaction of 1-methylimidazole and 2-chloro-4,6-dimethoxy-s-triazine is reported. The preparation of 2,4-dichloro-6-(2-pyridyl)-s-triazine via the synthesis of the pyridyl substituted triazine ring is also described.

1-Phenylpyrazole was lithiated[6] using one equivalent of n-butyllithium. The lithio derivative on reaction with cyanuric chloride at low temperature produced the expected 2,4-dichloro-6-(1-phenyl-pyrazol-5-yl)-s-triazine **1** in 30% yield. 3-Methyl-1-phenylpyrazole in a similar procedure gave only 12% of the 5-substituted pyrazole, 2,4-dichloro-6-(3-methyl-1-phenylpyrazol-5-yl)-s-triazine **2** and 3% of the *o*-phenyl substituted derivative, 1-[*o*-(2,4-dichloro-s-triazin-6-yl)phenyl]-3-methylpyrazole **3**, derived from lithiation of the ortho-position of the phenyl ring. A small amount (*ca.* 1%) of 2-methyl-9H-pyrazolo(1,5-a)-indole-9-one **4** was also isolated by chromatography, presumably derived from a reaction of dilithiated derivative with ambient $CO_2$. The analogous product from the dilithiated derivative of 1-phenylpyrazole and $CO_2$ is known.[7] The reaction of 3-methyl-1-phenylpyrazole directly with cyanuric chloride[18] in boiling nitrobenzene gave the expected Friedel–Crafts product,[8] 2,4-dichloro-6-(3-methyl-1-phenylpyrazol-4-yl)-s-triazine **5**, in *ca.* 14% yield.

No desired product was isolated from the reaction of a metalated derivative of 1-methylimidazole, thiazole, benzothiazole or pyridine with cyanuric chloride at −10 to −60° (in the cases of the lithio salts) or at 0 to −10° (in the cases of the Grignard reagents). Besides the apparent competing quaternisation reaction with the basic nitrogen of these heterocycles, it is also possible that the required products, once formed, can further undergo intermolecular quaternisation. We thus examined the direct reaction of cyanuric chloride with 1-methylimidazole. On adding 1-methylimidazole to a solution of cyanuric chloride in acetone, an instant precipitation of the product occurred. The IR (KBr) spectrum measured initially did not reveal any carbonyl absorption. The NMR spectrum in $D_2O$ solution showed a two-proton signal at $\delta$7·52 (m, $H_{4,5}$), 8·77 (m, $H_2$) and 3·99 (s, $NCH_3$), in good agreement with the reported values for 1-methylimidazole methiodide.[9] The product however, undergoes hydrolysis on standing as shown by the appearance of strong multiple C=O IR absorption bands at 1780–1720 $cm^{-1}$. A second set of NMR signals at $\delta$7·75 (t, $H_5$), 8·4 (t, $H_4$), 9·93 (m, $H_2$), 4·15 (s, $NCH_3$) also appears in addition to the above. This is presumably due to hydrolysis and becomes predominant in the completely hydrolysed product. The extra downfield shift of H-2 could be due to anisotropic deshielding by the neighbouring oxo-group of the triazine ring. Similar sets of signals due to unhydrolysed and hydrolysed components of approximate ratio 3:2 respectively in the product are also visible, when the reaction is carried out by reverse addition of the reagents. Mass spectrum (70 e/v) at 320° exhibited strong ions *m/e* 129, 82, 36, and



1: R = H, (pyrazol-5-yl)
2: R = $CH_3$, (pyrazol-5-yl)
5: R = $CH_3$, (pyrazol-4-yl)



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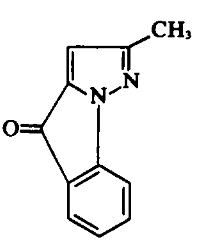

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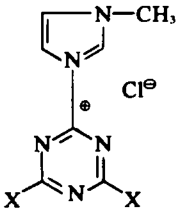
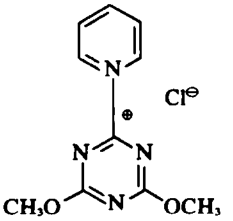


6: (X = Cl, $OCH_3$)



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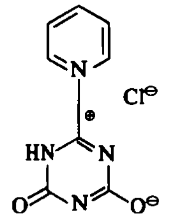

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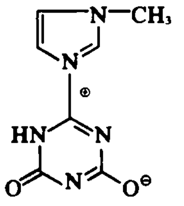

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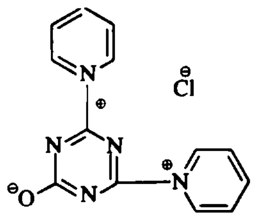

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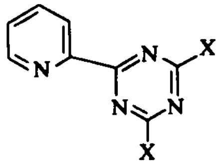

11: X = $SCH_2CH_3$
12: X = Cl

38 indicating the presence of cyanuric acid, 1-methylimidazole and hydrogen chloride respectively, suggesting initial formation of a quaternary imidazolium chloride (**6**, X=Cl), which undergoes gradual hydrolysis. The product, however, from the reaction of 2-chloro-4,6-dimethoxy-s-triazine and 1-methylimidazole was characterised to be the imidazolium chloride (**6**, X=$OCH_3$) by elemental analysis and spectral evidence. Similar reaction with pyridine led to the corresponding unstable pyridinium chloride (**7**). This on crystallisation from water afforded a product, which by analysis and spectral evidence, appears to be 1-(4,6-dihydroxy-s-triazin-2-yl)pyridinium hydroxide (inner salt) **8**, a compound reported[10] to have been obtained by reacting cyanuric chloride with pyridine in water. Similarly, crystallisation of 1-methylimidazolium chloride **6** from water led to a product which by analogy, as above, and spectral evidence, appears to be 1-methyl-3-(4,6-dihydroxy-s-triazin-2-yl)-imidazolium hydroxide (inner salt) **9**. Elemental analysis, however, indicated the presence of a mole of cyanuric acid and half a mole of water. The hydrated salts of cyanuric acid with bases and alkaloids are known,[11] but it is not clear how cyanuric acid is bound in the present case. The reaction of pyridine with cyanuric chloride in diethyl ether at −70° gave an unstable hygroscopic product, which on crystallisation from water produced the identical compound **8** (IR, analysis and m.p.). The structure of the intermediate product, by spectral evidence and analysis, appears to be a dipyridinium salt **10**.

In order to prepare 2,4-dichloro-6-pyridyl-s-triazine, we next turned to the synthesis of the triazine ring substituted with a pyridyl group linked to a C–C bond. This synthesis would lead to triazines having functional groups incorporating N,O, or S on the other carbon atoms. Except in the first instance, where a prior hydrolysis to the dioxo analogue is required, these groups can be halogenated[12] to give the dihalogeno-s-triazines. An attempt to make 2-(2-pyridyl)-s-triazin-4,6-(3*H*,5*H*)dione using the route[12] through acyldicyandiamide was not successful. An attempted hydrolysis of 2,4-diamino-6-(2-pyridyl)-s-triazine[13] with 20% aqueous HCl[14] gave only a non-separable mixture of the product and partially hydrolysed derivatives. However, the synthesis[15] of 2,4-dithioethyl-6-(2-pyridyl)-s-triazine **11** was achieved by reacting S,S′-diethyldithiobiuret with pyridine-2-carbonyl chloride or better with the mixed anhydride prepared from pyridine-2-carboxylic acid and ethylchloroformate. Treatment of **11** with chlorine in carbon tetrachloride solution gave the desired 2,4-dichloro-6-(2-pyridyl)-s-triazine **12** as its hydrochloride, which on neutralisation with sodium bicarbonate produced the base. A stable fluoroborate salt of this base was prepared. The hydrolytic stability of the free base was determined by UV spectroscopy.[16] At pH 7·72, a linear rate plot was obtained showing a half-life of 21 min but at pH 9·24, a curved rate plot was obtained, also a transient peak at 350 nm was observed. This is not consistent with the mechanism of hydrolysis observed in other dihalo-heteroaryl-s-triazines[17] and could possibly involve an intermediate quaternary complex.

## EXPERIMENTAL

Melting points were determined on a Kofler block under microscopic magnification or in capillary tubes and not corrected. The spectra were measured with Perkin–Elmer 457, Unicam SP800 and Varian A-60A spectrometers. Unless otherwise specified, IR spectra were for KBr discs, UV spectra for solutions in methanol and NMR spectra for solutions in deuteriochloroform (TMS as internal reference).

2,4 - *Dichloro* - 6 - (1 - *phenylpyrazol* - 5 - *yl*) - s - *triazine* **1**. 1-Phenylpyrazole (5·0 g, 0·035 mole) was lithiated[6] using 1 equivalent of n-BuLi in n-hexane. This reagent, under nitrogen, was added slowly to a well-stirred solution of cyanuric chloride (5·4 g, 0·03 mole) in dry benzene (100 ml) and diethyl ether (20 ml) at −10°. The mixture was stirred at room temperature overnight and evaporated to dryness under vacuum. The residue was extracted with n-hexane to give an oil, which on trituration with diethyl ether afforded the solid product, (3 g, 29·6%) m.p. 110–112° (n-hexane). $\nu_{max}$ 1600, 1520 cm$^{-1}$; δ($CCl_4$): 7·35 (d, $H_4$), 7·68 (d, $H_3$) ($J_{3,4}$ ≃ 1·7 Hz), 7·2–7·6 (5H, Ph); $\lambda_{max}$ 281 nm (log ε 4·22) (Found: C, 49·3; H, 2·4; N, 24·2; Cl, 24·5. $C_{12}H_7Cl_2N_5$ requires: C, 49·3; H, 2·4; N, 24·0; Cl, 24·3%).

2,4 - *Dichloro* - 6 - (3 - *methyl* - 1 - *phenylpyrazol* - 5 - *yl*) - s - *triazine* **2**. The lithiated reagent prepared[6] from 3-methyl-1-phenylpyrazole (4·78 g, 0·03 mole) was similarly reacted with cyanuric chloride (5·4 g, 0·03 mole) as described above. The reaction mixture was filtered and the filtrate evaporated under vacuum to a gum. This was extracted with hot n-hexane. The extract, on removal of solvent, was crystallised from benzene-n-hexane to give 1 - [*o* - (2,4 - *dichloro* - s - *triazin* - 6 - *yl*)*phenyl*] - 3 - *methylpyrazole* **3**. (0·3 g, 3%) mp 127–129°. $\nu_{max}$ 3130, 1602, 1580, 1520, 1480, 1450, 780, 712 cm$^{-1}$; NMR δ8·10 (1H, phenyl proton adjacent to triazinyl group), 7·4–7·7 (3H, Ph), 6·25 (1H, $H_4$), 7·60 (1H, $H_5$) $J_{4,5}$ ≃ 2·5 Hz (confirmed by decoupling), 2·20 (3H, C–$CH_3$); $\lambda_{max}$ 244 nm. (log ε 4·33) (Found: C, 51·0; H, 3·2; N, 22·7. $C_{13}H_9Cl_2N_5$ requires: C, 51·0; H, 3·0; N, 22·9%). The remaining product in the mother liquor was evaporated and the residue was dissolved in methylene chloride. The solution was chromatographed over a silica gel column eluting with benzene to give two fractions. (a) 2,4-Dichloro-6-(3-methyl-1-phenylpyrazol-5-yl)-s-triazine **2**, (1·1 g, 12%) m.p. 106–108°. $\nu_{max}$ 1598, 1520, 1490, 755, 690 cm$^{-1}$. NMR δ7·23 (m, $H_4$), 2·4 (3H, C–$CH_3$), 7·4 (m, 5H, Ph); $\lambda_{max}$ 287 nm (log ε 4·18) (Found: C, 51·2; H, 3·2; N, 22·7; Cl, 22·9. $C_{13}H_9Cl_2N_5$ requires: C, 51·0; H, 3·0; N, 22·9; Cl, 23·2%). (b) 2-Methyl-9H-pyrazolo(1,5-a)indole-9-one **4**, (0·1 g, 1%), m.p. 103–105°; $\nu_{max}$ 1720 (strong C=O), 755 cm$^{-1}$ (*o*-substituted phenyl); NMR δ6·47 (s, $H_4$), 2·37 (3H, s, C–$CH_3$), 7·1–7·7 (m, 4H, Ph); $\lambda_{max}$ 252 nm (log ε 4·44), 269 nm (log ε 4·03), 280 nm (log ε 4·01) (Found: C, 71·9; H, 4·44; N, 15·4. $C_{11}H_8N_2O$ requires: C, 71·7; H, 4·38; N, 15·2%).

2,4 - *Dichloro* - 6 - (3 - *methyl* - 1 - *phenylpyrazol* - 4 - *yl*) - s - *triazine* **5**. A mixture of 3-methyl-1-phenylpyrazole (0·52 g, 0·0033 mole) and cyanuric chloride 0·6 g, 0·0033 mole) in nitrobenzene (8 ml) was heated to reflux for 16 hr. Most of the solvent was removed under vacuum and the residue in benzene solution was passed through a short column of silica gel eluting with benzene to give the product, 0·15 g, (14%), m.p. 165–168° (benzene: n-hexane) $\nu_{max}$ 1595, 1530, 1465, 750, 685 cm$^{-1}$; NMR δ8·77 (1H, $H_5$), 2·70 (3H, C–$CH_3$), 7·3–7·8 (5H, Ph); $\lambda_{max}$ 312 nm (log ε 3·50). (Found: C, 51·1; H, 3·2; N, 23·1; $C_{13}H_9Cl_2N_5$ requires: C, 51·0; H, 3·0; N, 22·9%).

*Reaction of cyanuric chloride with* 1-*methylimidazole*. To a cold solution (ice bath) of cyanuric chloride (0·46 g, 0·0025 mole) in acetone (5 ml) (dried over molecular sieve) was added dropwise a solution of 1-methylimidazole (0·2 g, 0·0025 mole) in acetone (5 ml). The resulting precipitate was filtered, washed with acetone and dried under vacuum in a pre-heated oven at 60°; *ca.* 0·6 g $\nu_{max}$ 3155, 1450, 1340 cm$^{-1}$; soluble in water, an insoluble product, crystallised out from aqueous solution, on recrystallisation yielded a solid, *ca.* 0·3 g m.p. >310°; $\nu_{max}$ 1780–1720 cm$^{-1}$ (m, strong C=O); δ($CF_3COOD$): 9·67 (m, $H_2$), 8·35 (t, $H_4$), 7·69 (t, $H_5$), 4·20 (3H, $NCH_3$) (Found: C, 35·8; H, 2·90; N, 33·7; $C_7H_7N_5O_2$. $C_3H_3N_3O_3 \cdot \frac{1}{2}H_2O$ requires: C, 36·2; H, 3·34; N, 33·8%).

4,6 - *Dimethoxy* - 6 - (1 - *methyl* - 3 - *imidazolium*) - s - *triazine chloride* (**6**, X = $OCH_3$). To an ice cold solution of 2-chloro-4,6-dimethoxy-s-triazine[19] (1·75 g, 0·01 mole) in dry acetone (30 ml) was added dropwise a solution of 1-methylimidazole (0·82 g, 0·01 mole) in acetone (10 ml). The mixture was stirred for 24 hr at room temperature. The product was filtered, washed with acetone and dried under vacuum at 60°; *ca.* 1·8 g, (70%, hygroscopic solid); m.p. 290–296° (dec); $\nu_{max}$ 1610, 1555, 1510, 1480, 1375, 1260, 1195, 1140, 1100, 1085, 1040 cm$^{-1}$. δ($D_2O$): 10·07 (m, $H_2$), 8·48 (t, $H_4$), 7·93 (t, $H_5$) $J_{4,5}$ ≃ 1·5–2·0 Hz, 4·25 (s, 9H, 2-$OCH_3$, 1$NCH_3$); $\lambda_{max}$ 232 nm (log ε 3·85) (Found: C, 41·7; H, 4·97; N, 27·5; Cl, 13·9; O, 12·7; $C_9H_{12}ClN_5O_2$ requires: C, 41·9; H, 4·71; N, 27·2; Cl, 13·8; O, 12·4%).

*Reaction of pyridine with* 2 - *chloro* - 4,6 - *dimethoxy* - s - *triazine*. A similar reaction, as described above, was carried out with pyridine (0·4 g, 0·005 mole) and 2 - chloro - 4,6 - dimethoxy - s - triazine (0·88 g, 0·005 mole). The mixture on stirring at room temperature for 2 hr yielded a deliquescent solid 0·5 g (46%) 1 - (4,6 - dimethoxy - s - triazin - 2 - yl)pyridinium chloride **7**; dec >150°. $\nu_{max}$ 1620, 1555, 1470, 1360, 1255, 1195, 1145, 1095, 1030, 800, 710 cm$^{-1}$; δ($D_2O$): 10·2 (2H, $H_{2,6}$), 8·52 (2H, $H_{3,5}$); $J_{2,3}$ ≃ 5·5 Hz; 9·17 (1H, $H_4$): $J_{3,4}$ ≃ 8 Hz; 4·33 (6H, 2-$OCH_3$). On crystallisation from water, it afforded a solid which appeared to be identical with the reported 1-(4,6-dihydroxy-s-triazine-2-yl)pyridinium hydroxide inner salt **8**; m.p. >320° (lit[10] > 300°), $\nu_{max}$ 3350, 3020, 1680, 1610, 1565, 1450, 790, 725 cm$^{-1}$ (Found: C, 50·2; H, 3·31; N, 29·8; O, 16·4. $C_8H_6N_4O_2$ requires: C, 50·5; H, 3·18; N, 29·5; O, 16·8%).

*Reaction of pyridine with cyanuric chloride*. To a well stirred solution of cyanuric chloride (1·84 g, 0·01 mole) in dry diethyl ether (150 ml) cooled to −70° was added pyridine (0·79 g, 0·01 mole) in diethyl ether (20 ml). The resulting hygroscopic solid was filtered, washed with ether and dried in a vacuum dessicator, **10**, 1·8 g, m.p. 260° (dec) $\nu_{max}$ 3020, 1630, 1518, 1480, 1390, 800, 740 cm$^{-1}$. δ($D_2O$): 10·30 (m, 2H, $H_{2,6}$), 8·58 (m, 2H, $H_{3,5}$), 9·20 (m, 1H, $H_4$) $J_{2,3}$ ≃ 5·5 Hz, $J_{3,4}$ ≃ 8·0 Hz, $J_{2,4}$ ≃ 1·5 Hz. (Found: Cl, 12·14. $C_{13}H_{10}ClN_5O$ requires: Cl, 12·2%). The product on crystallisation from water gave the identical (IR and m.p.) compound **8** (Found: C, 50·3; H, 3·18; N, 29·4; O, 17·2. $C_8H_6N_4O_2$ requires: C, 50·5; H, 3·18; N, 29·5; O, 16·8%).

2,4 - *Dithioethyl* - 6 - (2 - *pyridyl*) - s - *triazine* **11**. Mixed anhydride was prepared in the normal manner from pyridine 2-carboxylic acid (5·0 g, 0·04 mole) and ethyl chloroformate (4·3 g, 0·04 mole) in THF solution in the presence of TEA (11·1 ml). $\nu_{max}^{THF}$ 1810, 1760 cm$^{-1}$. A solution of diethyldithiobiuret (7·6 g, 0·04 mole) in THF (10 ml) was added slowly to the above anhydride at 0°. The mixture was stirred at room temperature for 2 hr, evaporated to dryness under vacuum and the residue was dissolved in $CHCl_3$. The solution was washed with $NaHCO_3$ solution, dried ($Na_2SO_4$), and evaporated to an oil. This was chromatographed in n-hexane solution on neutral alumina, eluting with $CHCl_3$ to give a solid, which was crystallised from n-hexane, 2·8 g (25·2%), m.p. 62–64°. $\nu_{max}$ 1496, 1245 cm$^{-1}$. δ($CCl_4$): 8·75 (d dd, $H_6$), 8·41 (d dd, $H_3$), 7·88 (d dd, $H_4$), 7·37 (d dd, $H_5$), 3·23 (m, 4H, 2–$CH_2$–), 1·45 (m, 6H, 2–$CH_3$) $J_{3,4} = J_{4,5}$ = 7·5 Hz, $J_{5,6}$ = 5·5 Hz, $J_{4,6}$ = 1·9 Hz, $J_{3,5}$ = 1·6 Hz, $\lambda_{max}$ 266 nm (log ε 4·53). (Found: C, 51·9; H, 5·32; N, 20·1. $C_{12}H_{14}N_4S_2$ requires: C, 51·8; H, 5·06; N, 20·1%).

2,4 - *Dichloro* - 6 - (2 - *pyridyl*) - s - *triazine* **12**. To a solution of 2,4 - dithioethyl - 6 - (2 - pyridyl) - s - triazine (0·1 g) in dry $CCl_4$ (5 ml) was passed chlorine gas for 5 min at 35°. The resulting solid was filtered and dried in a vacuum dessicator, m.p. ~130° (dec.), insoluble in $CHCl_3$ but soluble in water; $\nu_{max}$ 3500–2500, 1602, 1505, 1322 cm$^{-1}$.

This was suspended in $CH_2Cl_2$ (5 ml) and neutralised with solid $NaHCO_3$; solution of filtration and evaporation yielded the base as a white solid, *ca.* 80 mg. $\delta$: 8·92 (d dd, $H_6$), 8·60 (d dd, $H_3$), 7·96 (d dd, $H_4$), 7·57 (d dd, $H_5$). $J_{3,4} = J_{4,5} = 8·0$ Hz, $J_{5,6} = 5·0$ Hz, $J_{3,5} = J_{4,6} = 1·5$ Hz, $J_{3,6} = 1·0$ Hz.

Fluoroborate, m.p. ~150° (subl.) (Found: C, 30·7; H, 1·64; N, 17·9; Cl, 22·4; F, 24·4; $C_8H_4Cl_2N_4 \cdot HBF_4$ requires: C, 30·5; H, 1·60; N, 17·8; Cl, 22·5; F, 24·1%).

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