then yielded 4.3 g. (50%) of slightly impure IIe, b.p. 50–65° at 35 mm. and 0.8 g. (7%) of 2,4-diethyl-*s*-triazine, b.p. 65–80° at 35 mm. Identification of these products was confirmed by comparison with infrared spectra of the authentic materials prepared by the reaction of formamidine hydrochloride with propionamidine hydrochloride.[5]

2-Benzyl-s-triazine (IIf). Ethyl 2-phenylacetimidate[6] (9.8 g., 0.060 mole) was added during 30 min. to a mixture of 3.2 g. (0.040 mole) of I, 0.30 g. of acetic acid, and 2.0 cc. of ethanol which was held at 50°. The reagents were then heated for 45 min. at 80°. Crystallization on cooling gave 0.30 g. of formamidine acetate, m.p. 157–158° (lit.[7] m.p. 162–164°). Distillation of the mother liquor yielded 2.4 g. (38%) of IIf, b.p. 135–145° at 25 mm. (lit.[2] b.p. 100–105° at 2 mm.), and recrystallization of the residue from methanol gave 0.65 g. (7%) of 2,4-dibenzyl-*s*-triazine, m.p. 71–73° (lit.[2] m.p. 80–82°). Infrared comparison showed that these products were essentially identical with authentic samples prepared by the reaction of 2-phenylacetamidine hydrochloride with I[2].

2-Phenyl-s-triazine (IIb). *s*-Triazine (4.05 g., 0.050 mole) was heated with 14 g. (0.10 mole) of 97% methyl benzimidate at 100–110° for 20 hr. Following this no IIb was detectable by infrared. Ethanol (2.5 cc.) was then added and the mixture was heated at reflux for 4 hr. A small amount of IIb was then evident. Addition of 0.10 cc. of acetic acid and 8 hr. longer at 80° caused marked reduction in the imidate content of the solution, which was then diluted with water and extracted with ether. Evaporation of the ether and distillation of the residue gave 5.6 g. of IIb, b.p. *ca.* 105° at 2 mm., m.p. 62–64° (lit.[2,8] m.p. 63–65°), and 1.5 g. of less pure material as still holdup. The crude yield was thus 0.047 mole or 94%. The product was identical with authentic material by infrared comparison.

2-m-Nitrophenyl-s-triazine (IIc). A reaction mixture consisting of 8.9 g. of 93% methyl *m*-nitrobenzimidate[9] (0.046 mole), 3.80 g. (0.047 mole) of I, 0.60 g. (0.010 mole) of acetic acid, and 10 cc. of ethanol was heated at reflux for 3 hr. Essentially pure IIc crystallized as the reaction mixture cooled; yield, 7.6 g. (82%), m.p. 122–128°. Recrystallization from toluene gave material melting at 127–129° which was identical with IIc prepared by reaction of I with *m*-nitrobenzamidine hydrochloride.[2,11]

2-p-Nitrophenyl-s-triazine (IId). A mixture of 8.2 g. of 79% ethyl *p*-nitrobenzimidate[12] (0.033 mole), 3.0 g. (0.037 mole) of I, 0.45 cc. (0.0075 mole) of acetic acid, and 7 cc. of ethanol was heated at reflux for 3 hr. Crystals formed as the reaction proceeded. Filtration of the crude product and washing with ethanol gave 4.5 g., m.p. approx. 160°. Extraction of the solid with toluene left a slight amount of insoluble by-product. Fractional crystallization of the extract yielded 2.8 g., m.p. 166–168° (42%). Recrystallization from cyclohexane or toluene raised the melting point to 167–169°.

Anal. Calcd. for $C_9H_6N_4O_2$: C, 53.46; H, 2.99; N, 27.72. Found: C, 53.70; H, 2.95; N, 27.43.

Dilution of the ethanolic mother liquor from the reaction mixture with water caused crystallization of 3.4 g., m.p. 50–60°. Titration of this material showed it to be 71% ethyl *p*-nitrobenzimidate (40% recovery).

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(6) A. Pinner, *Die Imidoäther und ihre Derivate*, Robert Oppenheim (Gustav Schmidt), Berlin, Germany, 1892, p. 155. The imidate distilled at 110–112° at 22 mm. without apparent decomposition.

(7) E. C. Taylor and W. A. Ehrhart, *J. Am. Chem. Soc.*, **82**, 3138 (1960).

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(9) Methyl *m*-nitrobenzimidate was prepared by the general procedure of ref. 10. Recrystallization of the crude product from ether gave material which was 93% pure by titration, m.p. 50–51°.

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(11) The melting point of pure IIc was omitted from reference 2. The analytical sample was recrystallized from aqueous acetonitrile and had m.p. 129–130°.

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[CONTRIBUTION FROM THE ORGANIC CHEMICALS DIVISION, RESEARCH DEPARTMENT, MONSANTO CHEMICAL CO.]

Unsymmetrically Substituted Melamines

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Unsymmetrically substituted melamines have been prepared from cyanuric chloride by successive reaction with three different amines. The procedure is quite general. Most of these new compounds are liquids and were found to possess a rather high degree of thermal stability.

In the course of a search for thermally stable compounds, particularly those with wide liquid ranges, our attention was turned to melamine and its derivatives. These substances should be inherently stable as many of them possess very high melting points and melt without decomposition.[1-3] Furthermore, the *s*-triazine nucleus is similar to the very stable benzene ring.

Increasing substitution on the three exocyclic nitrogen atoms of melamine results in a corresponding lowering of melting points.[4] We proposed that the completely unsymmetrical melamines in which the three substituted amino groups are all different should have relatively low melting points and might even be liquids at room temperature. Nineteen of these compounds have been synthesized and the majority are liquids (*cf.* Table I).

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(2) J. T. Thurston *et al.*, *J. Am. Chem. Soc.*, **73**, 2981 (1951); D. W. Kaiser *et al.*, *J. Am. Chem. Soc.*, **73**, 2984 (1951); J. R. Dudley *et al.*, *J. Am. Chem. Soc.*, **73**, 2986 (1951).

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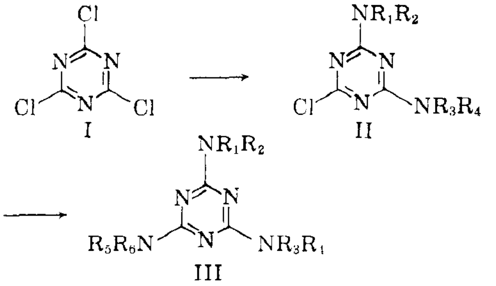
TABLE I

UNSYMMETRICALLY SUBSTITUTED MELAMINES (III)

No.	R_1	R_2	R_3	R_4	R_5	R_6	M.P., B.P. (Mm.)	Yield, %	State
IV	H	C_3H_7	H	C_4H_9	H	C_6H_{13}	175–180 (0.3)	93	Liquid
V	H	C_3H_7	H	C_4H_9	H	C_8H_{17}	200–214 (0.5)	88	Liquid
VI	H	C_4H_9	H	C_6H_{13}	H	C_6H_{11}	205–215 (0.4)	89.5	Liquid
VII	H	C_4H_9	H	C_6H_{13}	H	C_6H_5	225–230 (0.08)	88	Glass
VIII	H	C_3H_7	H	C_4H_9	H	$(CH_3)_3SiCH_2$	161–170 (0.25)	76	Liquid
IX	H	C_6H_{13}	H	C_6H_5	H	$C_6H_5CH_2$	258–268 (0.4)	93	Glass
X	H	C_4H_9	H	C_6H_5	H	p-$CH_3C_6H_4$	245–255 (0.25)	80	Solid[a]
XI	H	C_6H_{13}	H	C_6H_5	$-CH_2CH_2OCH_2CH_2-$		235–240 (0.35)	89	Liquid
XII	H	C_4H_9	$(CH_2)_4$		$-CH_2CH_2OCH_2CH_2-$		182–190 (0.25)	90	Liquid
XIII	$(CH_2)_4$		$(CH_2)_5$		$-CH_2CH_2OCH_2CH_2-$		187–188	82	Solid[b]
XIV	H	m-$CH_3C_6H_4$	H	p-BrC_6H_4	H	2,4-$(CH_3)_2C_6H_3$	153	87	Solid[c]
XV	H	C_6H_{13}	H	C_6H_5	C_4H_9	C_4H_9	212–225 (0.25)	92.5	Liquid
XVI	H	C_4H_9	C_4H_9	C_4H_9	$(CH_2)_5$		187–189 (0.4)	94	Liquid[d]
XVII	H	C_4H_9	H	C_6H_{13}	$C_6H_5CH_2$	$C_6H_5CH_2$	250–256 (0.7)	70	Liquid[e]
XVIII	H	C_4H_9	C_2H_5	C_2H_5	C_4H_9	C_4H_9	165–170 (0.4)	89.5	Liquid[f]
XIX	CH_3	CH_3	C_2H_5	C_2H_5	C_3H_7	C_3H_7	127–135 (0.8)	87	Liquid[g]
XX	C_2H_5	C_2H_5	C_3H_7	C_3H_7	C_4H_9	C_4H_9	147–160 (0.35)	77	Liquid[h]
XXI	C_3H_7	C_3H_7	C_4H_9	C_4H_9	C_6H_{13}	C_6H_{13}	195–215 (0.7)	99	Liquid[i]
XXII	C_2H_5	C_2H_5	C_6H_5	C_6H_5	$C_6H_5CH_2$	$C_6H_5CH_2$	250–270 (0.5)	9	Glass[e,j]

[a] M.p. 72–74°. [b] From petroleum ether (b.p. 77–115°). [c] From ethanol. [d] n_D^{25} 1.5246. [e] Solidified on standing. [f] n_D^{25} 1.5086. [g] n_D^{25} 1.5157. [h] n_D^{25} 1.5010. [i] n_D^{25} 1.4940. [j] n_D^{25} 1.6183.

The melamines (III) were prepared from cyanuric chloride (I) by a procedure similar to one developed in another laboratory.[2]



The intermediate monoamino derivatives were not isolated, but the diamino compounds, II, were insoluble in the reaction medium. They were isolated and in most cases were used without purification. A different solvent system, n-butyl alcohol, was employed in the final step (II → III) for the introduction of the last amino function.

Because of weak nucleophilicity and large steric requirements diphenyl amine failed to react with the diethylaminodibenzylamino-s-triazine (II. $R_1 = R_2 = C_2H_5$; $R_3 = R_4 = C_6H_5CH_2$). The desired product, XXII, was then obtained from 2-diphenylamino-4,6-dichloro-s-triazine[2] by successive treatment with diethyl and dibenzylamines.

Most of the unsymmetrically substituted melamines are liquids ranging from mobile oils to glasses at room temperature, confirming our expectations. Cyclic substituents tend to increase the viscosity or produce solids.

TABLE II

THERMAL STABILITY DATA

Compound	Weight Loss, %
IV	4.9
V	3.9
X	2.7
XVI	4.8
XX	7.8
Trimethylolpropane tri(α,α-dimethylvalerate)	14.6
Diphenyldidodecyl silane	13.7
Bis(m-phenoxyphenyl) ether	1.5
Bis(1-methylcyclohexylmethyl) sebacate	5.1
Mixed polyalkylbenzenes	10.8
Silicone (G.E. Versilube F-50)	3.6
Di(2-ethylhexyl)sebacate	Dec.

Many of the melamines proved to be very stable thermally. Test results indicate that they compare favorably with other materials (*cf.* Table II), which have been suggested for use as hydraulic fluids, synthetic lubricants, heat exchanger media, radiation resistant fluids, etc. Compound X approaches the stability of the polyphenyl ethers which have attained commercial importance.

Thermal stabilities of the compounds in Table II were determined in the following way: tubes containing test samples under nitrogen were immersed in the vapors of refluxing Aroclor 1254 for ten hours. Vapor temperature was maintained at 371°. Provisions were made to collect distillate and any gases, if desired. Following the heating period, changes in weight and appearance of the sample together with the amount of distillate were determined. This simple and convenient screening test has been useful in providing comparative data.

TABLE III

Analytical Results for Unsymmetrically Substituted Melamines

No.	Formula	Carbon, %		Hydrogen, %		Nitrogen, %	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
IV	$C_{16}H_{32}N_6$	—	—	—	—	27.25	27.42
V	$C_{18}H_{36}N_6$	64.24	64.23	10.78	10.47	24.98	25.23
VI	$C_{19}H_{36}N_6$	65.47	64.93	10.41	10.03	24.11	24.99
VII	$C_{19}H_{30}N_6$	66.63	65.92	8.83	8.60	24.54	24.71
VIII	$C_{14}H_{30}N_6Si$	—	—	—	—	27.07	26.53
IX	$C_{22}H_{28}N_6$	—	—	—	—	22.33	22.29
X	$C_{20}H_{24}N_6$	68.94	68.56	6.94	7.05	24.12	24.50
XI	$C_{19}H_{28}N_6O$	—	—	—	—	23.58	23.70
XII	$C_{15}H_{26}N_6O$	58.79	58.08	8.55	8.54	27.43	26.89
XIII	$C_{16}H_{26}N_6O$	60.35	60.67	8.23	8.07	26.40	26.41
XIV	$C_{24}H_{23}BrN_6$	—	—	—	—	17.68	17.64
XV	$C_{23}H_{38}N_6$	69.30	68.68	9.61	9.43	21.08	21.35
XVI	$C_{20}H_{38}N_6$	—	—	—	—	23.18	23.30
XVII	$C_{27}H_{38}N_6$	—	—	—	—	18.82	19.31
XVIII	$C_{19}H_{38}N_6$	65.10	64.22	10.93	10.43	23.98	23.76
XIX	$C_{15}H_{30}N_6$	—	—	—	—	28.54	28.65
XX	$C_{21}H_{42}N_6$	66.22	66.74	11.18	10.88	22.20	22.76
XXI	$C_{29}H_{58}N_6$	—	—	—	—	17.13	16.65
XXII	$C_{33}H_{34}N_6$	77.01	76.49	6.66	7.01	16.33	16.43

EXPERIMENTAL[5]

General procedure for synthesis of diaminochloro-s-triazines (II). A slurry was prepared by running a thin stream of 0.2 mole of cyanuric chloride dissolved in 80 ml. of hot acetone into 170 ml. of ice-cold water. To this slurry at 0–5° was added 0.2 mole of the first amine[6] followed by 0.2 mole of sodium hydroxide dissolved in 15–20 ml. water at such a rate that the temperature never exceeded 5°. When the additions were complete, the mixture was stirred for one hour at ice bath temperatures. Then 0.2 mole of the second amine was introduced under the same conditions employed for the first addition. However, the ice bath was removed and the reaction mixture allowed to warm up during addition of the second aqueous portion of 0.2 mole of sodium hydroxide. Following this treatment the reaction temperature was raised to 45–50° which was maintained for 5–6 hr. The mixture was cooled to room temperature and the diaminochloro compound, insoluble in the aqueous acetone, was separated either as an oil or a solid. The product was washed with water and in most cases used in the subsequent reaction without further purification.

2-Diethylamino-4-di-n-propylamino-6 chloro-s-triazine (II. $R_1 = R_2 = C_2H_5$, $R_3 = R_4 = C_3H_7$). According to the above method 0.5 mole each of cyanuric chloride, diethylamine, and di-*n*-propylamine gave 138.1 g. (96.5%) of colorless oil, b.p. 132–135° (0.6 mm.).

Anal. Calcd. for $C_{13}H_{24}ClN_5$: Cl, 12.41; N, 24.5. Found: Cl, 12.63; N, 23.75.

2-Di-n-propylamino-4-di-n-butylamino-6-chloro-s-triazine (II. $R_1 = R_2 = C_3H_7$, $R_3 = R_4 = C_4H_9$). Following the same method a quantitative yield of colorless oil, b.p. 150–165° (1 mm.), was obtained from one mole each of cyanuric chloride, di-*n*-propylamine and di-*n*-butylamine.

Anal. Calcd. for $C_{17}H_{32}ClN_5$: N, 20.48. Found: N, 20.19.

General procedure for synthesis of melamines (III). A mixture consisting of 0.2 mole of the diaminochloro intermediate (from above) and 200 ml. of *n*-butyl alcohol was heated to 90–95°. During this heat-up period when the bath temperature was 55-60°, 0.2 mole of the final amine was added rapidly. At 90–95° addition of 0.2 mole of aqueous sodium hydroxide was started. It was added at such a rate that the reaction mixture remained just alkaline to phenolphthalein or alkacid test paper. When all had been added, heating at 90–95° was continued for 3-4 additional hr. The two-phase liquid system was allowed to cool to room temperature and the alcoholic layer separated from the aqueous base. The alcoholic layer was washed with water and the solvent removed under reduced pressure. The liquid residue was vacuum distilled, giving a high yield of oil or glass. In only two cases did the latter solidify, but in two others a solid was obtained as a residue following solvent removal. These were purified through recrystallization.

Yields and properties of these new compounds are given in Table I. Table III reports the analyses.

N^2-Diethyl-N^4-diphenyl-N^4-dibenzylmelamine (XXII) To a slurry of 184 g. (1 mole) of cyanuric chloride in 500 ml. acetone — 900 ml. water at 0–5° was rapidly added 170 g. (1 mole) of diphenylamine. The ice cold mixture was stirred for 30 min., 106 g. (1 mole) of sodium carbonate added slowly and stirring continued for 2 hr. at room temperature. Ether was added to the cooled mixture and part of the precipitated solid dissolved. The insoluble portion was collected, weighed 71,2 g., and melted at 174–175°. Recrystallization from ethanol raised the melting point to 191–192°. The ether-soluble solid was isolated and recrystallized from ethanol yielding 74.2 g. of a white solid, m.p. 165–170°.

Total yield of the diphenylaminodichloro-s-triazine was taken as 155.4 g. (49%). The literature[3] reports: m.p. 172–174° and yield 85%.

A mixture of this intermediate and 500 ml. of *n*-butyl alcohol at 0–5° was treated with 35.8 g. (0.49 mole) of diethylamine followed by 0.49 mole of aqueous sodium hydroxide. Temperature was allowed to rise during the latter addition and finally was raised to 45–50° for several hours. The white crystalline diaminochloro intermediate separated. Then, 96.5 g. (0.49 mole) of dibenzylamine was introduced followed by 0.49 mole of aqueous sodium hydroxide. Reaction temperature was increased to 90–95° where it was held for 10 hr. After cooling to room temperature, the layers were separated, and the alcohol layer washed with water. The solvent was distilled, followed by the residue which gave 86.5 g. of dibenzylamine; 72.6 g. of viscous oil, b.p 200–215° (0.5 mm.), solidified on standing; and 45.2 g. (9%) of a glass, b.p. 250–270° (0.5 mm.), n_D^{25} 1.6188. The latter was the desired product whose infrared spectrum was quite similar to those of other known substituted melamines.

Recrystallization of the solid from methanol yielded

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(5) All melting and boiling points are uncorrected.

(6) Lower boiling amines were usually introduced at the lower reaction temperatures in order that losses due to volatility might be minimized.

white crystals, m.p. 90–91°. The infrared spectrum of this substance was also typical of substituted melamines. This together with the analyses indicated that the solid is N^2-diphenyl-N^4,N^6-bis(diethyl)melamine.

Anal. Calcd. for $C_{22}H_{30}N_6$: C, 70.73; H, 7.74; N, 21.52 Found: C, 70.88; H, 7.90; N, 21.28.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF SAN DIEGO STATE COLLEGE]

Acidity Constants of Some Arylimidazoles and Their Cations

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A comparative study of the thermodynamic acidity constants, both $pK°_a$ and $pK°_{a+}$, of imidazole, the mono- and di-C-phenylimidazoles, benzimidazole, and 2-phenylbenzimidazole is presented.

This paper is a continuation of our study of the effect of phenylation on the acidity of some amphiprotic arylimidazoles. In our earlier work[1,2] the acidity of the neutral molecules was studied; in this work their basicity or the acidity of their cations is considered. Of interest here is the effect of protonation on the role of the phenyl group. Added to the list of compounds studied is 4,5-diphenylimidazole, which, with phenyl groups on adjacent carbons, is of steric interest. To favor the cancelling out of procedural and systematic errors when making comparisons by difference, we have determined all acidity constants but one in our laboratory. The value not determined was that for the cation of imidazole which was not amenable to study by the method used.

EXPERIMENTAL

Calculation of the thermodynamic constants. The negative logarithm of the thermodynamic acidity constant of the neutral molecules, $pK°_a$, was calculated from the experimentally determined hydrolysis constants of the anions by the known relationship

$$pK°_a = pK°_w - pK°_h \qquad (1)$$

where $K°_w$ is the thermodynamic ionization product of water and $K°_h$ the thermodynamic hydrolysis constant of the anion. We have shown[1] that with 2-phenylbenzimidazole there is, within error of measurements, a linear relationship between pK_h and ionic strength, I_c, given by the equation

$$pK_h = pK_h° - mI_c^{1/2} \qquad (2)$$

where m is the slope. Following the same procedures that were used with 2-phenylbenzimidazole, we find that benzimidazole and 2,4(or 2,5)-diphenylimidazole give a slope of 0.10 which is the same slope to two significant figures found for 2-phenylbenzimidazole. For 4,5-diphenylimidazole the experimentally determined slope is 0.11. The probable error in the measured slopes is 0.02. Equation 2 was used to calculate $pK°_h$ for use in Equation 1 in every instance. The effect of ionic strength on the pK_h of imidazole and the mono-C-phenylimidazoles was not determined by experiment, and their $pK°_h$ was calculated using 0.10 for m and the reported pK_h values. The pK_h values for 4,5-diphenylimidazole, not previously reported, were obtained in the same manner as that described for the other arylimidazoles. The probable error in the $pK°_a$ values of this work is 0.04 pK units except for the $pK°_a$ of imidazole where the probable error is 0.06 pK units.

The negative logarithm of the thermodynamic acidity constant of the cations, $pK°_{a+}$, is given by the equation

$$pK°_{a+} = pH + \log c_{RH_2^+}/c_{RH} + \log \gamma_{RH_2^+}\gamma_{H_2O}/\gamma_{RH} \qquad (3)$$

The concentrations of the cation, $c_{FH_2}{}^+$, and of the nonion, c_{RH}, were determined spectrophotometrically.[3] The neutral. molecule's spectrum was measured in a 0.02*M* National Bureau of Standards pH 9.18 borax buffer. The aqueous solutions were acidified with hydrochloric acid to appropriate pH's for the equilibrium absorbancy measurements and the spectrum of the cation. The pH was measured with a Beckman Model G pH meter equipped with glass and calomel electrodes. The pH meter was calibrated with a 0.025*M* National Bureau of Standards pH 6.86 phosphate buffer at 25° ± 0.2. The reported $pK°_{a+}$ values are averages from measurements at three different pH's, and the $pK°_{a+}$ obtained at each pH is in turn the average from measurements at five or more wave lengths. The probable error is 0.03 pK units. We have neglected the activity coefficient term in Equation 3, since the total ionic strength of the solutions used in our equilibrium measurements was less than 10^{-4} g. ions/l.

Spectral data. All spectral measurements were made with a Model DU Beckman spectrophotometer. One-centimeter cells were used in every case except for 4,5-diphenylimidazole where 10-cm. cells were used. The temperature in the cell compartment was maintained at 25° ± 0.2 with Beckman thermospacers. Readings were corrected for any differences in the absorbancies of the two cells when filled with water.

Preparation of compounds. 4,5-Diphenylimidazole was prepared according to Davidson, *et al.*[4]; the other compounds were prepared as indicated in our earlier reports.[1,2]

RESULTS AND DISCUSSION

In Table I are given the thermodynamic acidity constants of the neutral molecules and their cations. To facilitate comparison between the two series of constants, a graph of $pK°_{a+}$ as abscissa and $pK°_a$ as ordinate, with a reference line of unit slope drawn arbitrarily through imidazole, is shown in Fig. 1.

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