The Influence of Methyl Group Substitution on the Odour of Aliphatic Nitriles

By C. S. Sell and P. Cairns, PPF International Ltd., Ashford, Kent, England

As part of an investigation into structure/odour correlations, we decided to synthesise a matrix of nitriles consisting of three series; viz, unsubstituted, 2-methyl substituted, and 3-methyl substituted; with five members (i.e., C_8 to C_{12} chains*) in each series, in order to determine the effects, if any, of methyl substitution on odour.

All of the nitriles in question were synthesised from readily available starting materials as shown in figure 1. The unsubstituted series were prepared by dehydration of the corresponding oximes; the 2-methyl nitriles from the corresponding methyl ketones using tosyl methyl iso-cyanide (TosMIC) according to the method of van Leusen[1]; and the 3-methyl nitriles by condensation of the corresponding methyl ketone with cyanoacetic acid followed by decarboxylation and hydrogenation of the resultant cyanoacid. All of the materials produced in this way possessed physical and spectroscopic properties consistent with those expected for the desired structures.

The fifteen nitriles were distilled and/or chromatographed to a high degree of purity and evaluated at various concentrations by a number of perfumers. The resultant odour descriptions are shown in Table I from which it is clear that both chain length and methyl group substitution pattern affect the odour character and strength of aliphatic nitriles.

Those nitriles with a C_8 chain have high impact, low tenacity and more nutty/lactonic character than the higher homologues. The C_9 nitriles have lower impact than the C_8 and C_{10} analogues with softer, more subtle characters and increased peachy notes. In fact, the peach character apears to be at a maximum in the C_9 member in each series. The higher homologues, i.e., C_{10}-C_{12}, have more fresh and citrus character with impact decreasing and tenacity increasing in proportion to chain length. Freshness also increases with chain length in both the n- and 3-methyl series but is more dominant in the latter where it becomes evident in 3-methylnonanonitrile.

The unsubstituted nitriles, compared to their methyl substituted counterparts, are somewhat harsher with more lactonic, aldehydic and nitrilic character. The 2-methyl substituted nitriles are much softer and possess pronounced florality—mainly of the jasmin type, although 2-methylundecanontrile is more reminiscent of lilac than jasmine—with peachy undertones. The 3-methyl substituted nitriles have distinct, fresh, citrus and green notes superimposed on a jasminic/floral background.

The importance of the green notes in the odours of the materials in this series is particularly surprising since it is a feature which is almost completely absent from the other two. On

* Throughout this article Cx refers to a nitrile with x carbon atoms in the main chain and not to the total number of carbon atoms.

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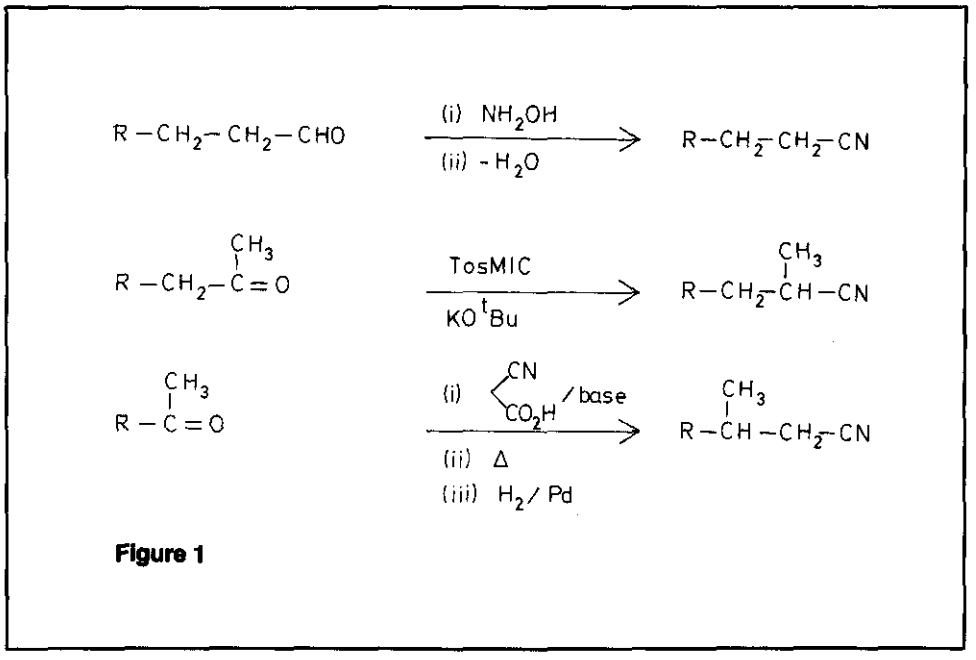


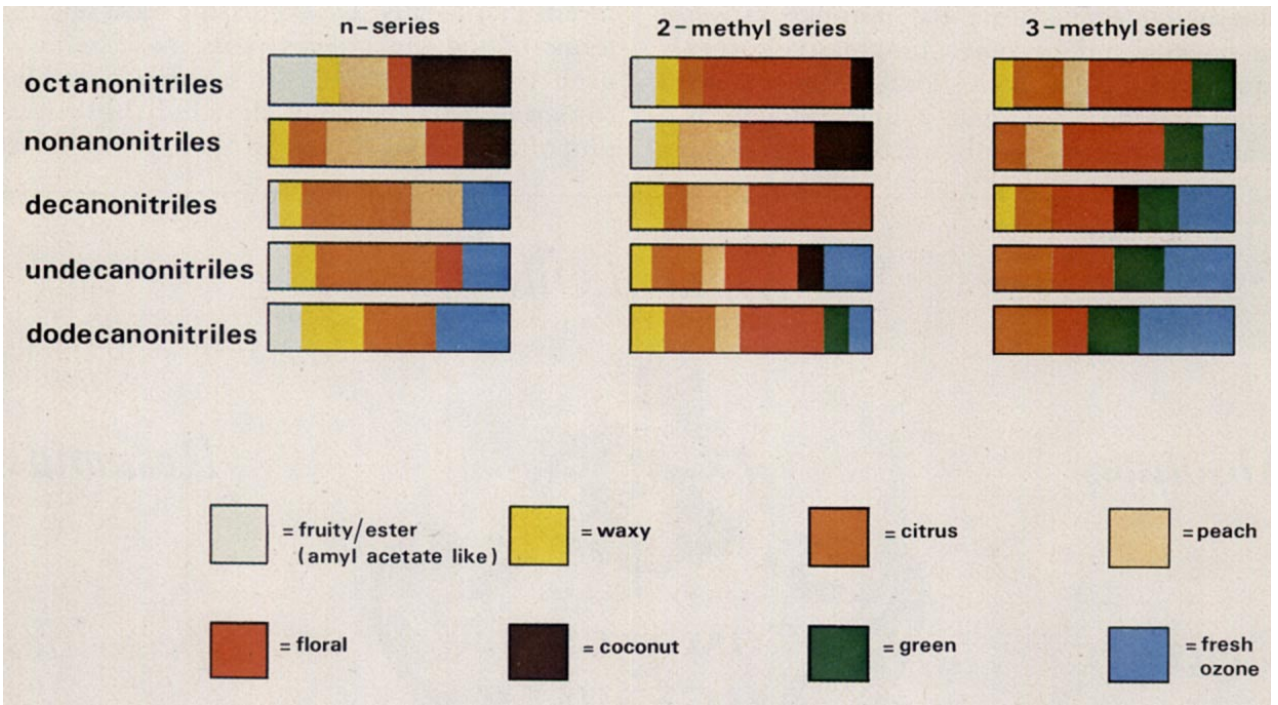
Figure 1

ascending the series from 3-methyloctanonitrile to 3-methyldodecanonitrile the jasminic aspect of the background becomes progressively less prominent while the fresh, floral and citrus aspects become more so. Again, a lilac character is evident in the eleven membered chain.

Figure 2 is an attempt to represent those trends graphically. By expressing their odours in terms of the eight descriptors most frequently used to describe them, it became possible to construct bar diagrams showing the relevant proportions of each facet of the odour character

Table I. Odour Descriptions of Aliphatic Nitriles

chain length / substitution	octanonitrile	nonanonitrile	decanonitrile	undecanonitrile	dodecanonitrile
n-	Fruity ester, amyl acetatelike topnote. Main body is lactonic with peach and coconut notes - somewhat reminiscent of nonalactone. Intense odour with great impact	Less impact than octanonitrile. The character is lactonic with the peach notes stronger and the nutty notes weaker than those of octanonitrile	Aldehydic/nitrilic type character with with some waxy peach notes	Aldehydic, almost ozonelike, fresh with decylaldehyde type orange notes, some mandarin character. Very persistent	Aldehydic, fresh ozone, some orange character. Rather weak but very long lasting
2-methyl-	Floral jasminic character with some celery aspects and a hint of coconut/lactone - very diffusive	Soft, floral, lactonic, jasmine/peachy character	A fine/light jasmine/floral character with a soft peachy quality	Fresh, floral with some lilac character. Tenacious	Soft, floral, with a green jasminic type odour, very persistent
3-methyl-	An unusual floral type consisting of a distinct fatty jasminic character combined with an agrumen quality	Fresh, jasminic floral type with a slightly green quality	Soft, citrus floral, reminiscent of jasmine	Light, fresh, green, floral, suggesting lilac with slight citrus undertones	Distinct orange character which is suffused by a light green seafresh quality



of the individual nitriles. Obviously, the weightings given are arbitrary and varied from one perfumer to another; however, these 'average' figures do serve to illustrate the patterns which exist.

Conclusion

The interesting odour properties of methyl substituted nitriles, coupled with the typical stability/safety properties of nitriles[2] suggest that they will become valuable perfumery materials. Appropriate patent protection covering these materials has been applied for.

Acknowledgement

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References

1. O. H. Oldenziel, D. van Leusen and A. M. van Leusen, J. Org. Chem. **42**, 3114, 1977
2. R. DeSimone, Perf. Flav. **4** (6), 1, 1980