Studies in nitrosopyrazoles. Part 1. Preparative and spectroscopic studies of some 3,5-dialkyl-4-nitrosopyrazoles

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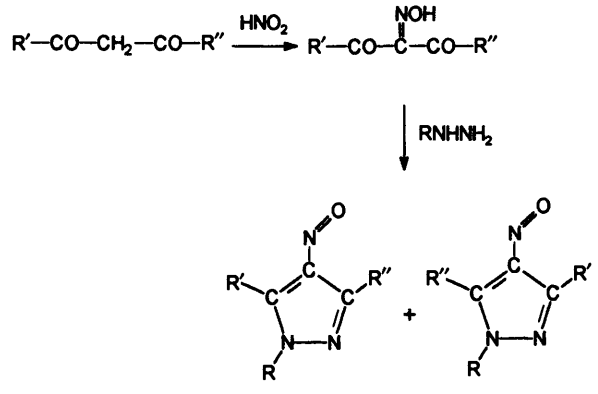
The preparations of a number of 3,5-disubstituted- and 1,3,5-trisubstituted-4-nitrosopyrazoles are described and a range of physical properties of these compounds are measured. Comparison is made with some 2,6-disubstituted nitrosobenzenes and it is shown from ^{13}C NMR spectroscopy that the effects of substitution by flanking *tert*-butyl groups are moderated in the case of the pyrazoles from those in the aromatic C_6 ring due to a lessening of steric hindrance. It is also suggested that steric effects are evident in the preparation of 1,3,5-substituted-4-nitrosopyrazoles when one of the flanking groups to the NO is *tert*-butyl or phenyl, there being no such effect for the corresponding case of the isobutyl group.

Although 4-nitrosopyrazoles have been known for over 90 years,[1] relatively little spectroscopic information is available, being confined primarily to a study of the electronic absorption spectrum of 3,5-dimethyl-4-nitrosopyrazole in water and in dilute sodium hydroxide.[2] Preparations of a number of 1-H-3,5-dialkyl(or diaryl)-4-nitrosopyrazoles and 1,3,5-trisubstituted-4-nitrosopyrazoles have been reported[3-8] and a small number of nitrosopyrazoles have been found to form nitroxides when used as spin traps.[9-12]

The generally favoured preparative route for 4-nitrosopyrazoles involves the nitrosation of β-diketones to give the oxime followed by condensation with either hydrazine or a mono-substituted hydrazine to give the corresponding 1-H- or 1-R-3(5)-R'-5(3)-R''-4-nitrosopyrazole (see Scheme 1). The



Scheme 1

literature gives little or no consideration to factors which control the relative proportions of the two isomers.

There is no evidence for any occurrence of dimerisation in the 4-nitrosopyrazoles and in this, as in other structural features, there are similarities with the substituted nitrosobenzenes 4-RR'N-C_6H_4-NO. It therefore seemed desirable to extend our spectroscopic studies to the 3,5-dialkyl-4-nitrosopyrazoles. Of further interest is the possible comparison between the 3,5-di-*tert*-butyl-4-nitrosopyrazole and 2,4,6-tri-*tert*-butyl-nitrosobenzene[13] and 2,6-di-*tert*-butylnitrosobenzene[14] with regard to the steric effects of the bulky alkyl groups upon the NMR chemical shift of the *C*-NO carbon. The geometry of the five-membered ring of the nitrosopyrazole implies that the steric hindrance of the nitroso group by the adjacent *tert*-butyl groups will be reduced compared with that for the similarly hindered nitrosobenzene. The ^{13}C substituent chemical shift (SCS) of the NO group is increased considerably[15] when it is flanked by the bulky *tert*-butyl groups attached to the benzene ring.

Experimental

Instrumental

^1H NMR spectra were measured using either a Bruker WP200 spectrometer operating at 200 MHz or at 60 MHz using a JEOL PMX 6051 spectrometer, the solvent being $CDCl_3$, CCl_4, CD_3OD or $(CD_3)_2CO$. Natural abundance, broad band proton-decoupled ^{13}C NMR spectra were measured on the Bruker instrument operating at 50.32 MHz, the solvents being $CDCl_3$, $(CD_3)_2CO$, or CD_3OD. Dipole moments were measured using a WTW Dipolmeter DM01, using the solvent 1,4-dioxane. In all cases solutions of five different concentrations (5, 4, 3, 2, 1% m/m) were employed and the relative permittivity and refractive index of each solution was measured. The method of Hederstrand,[16] Guggenheim[17] and Smith[18] was used to obtain the dipole moment from these measurements. Mass spectra were measured at 15 eV using a source temperature varying between 160 and 180 °C. Relative intensity values are given for all peaks greater than 10% of that of the largest peak given as 100.

Preparations

WARNING. In view of comments by New and Sundholm[3] concerning skin irritation and rashes in some cases of exposure to 4-nitrosopyrazoles and similar experience by one of us (M. C.), it is strongly advised that appropriate protection to the hands and face be taken with all of these compounds.

The nitrosopyrazoles synthesised and studied are listed in Table 1.

3,5-Dimethyl-4-nitrosopyrazole (1). Acetylacetone (10 g, 0.1 mol) was added to a solution of concentrated hydrochloric acid (9 ml) in 50 ml water and cooled in ice to 8 °C. Sodium nitrite (7.1 g, 0.1 mol) in 20 ml water was added dropwise and the mixture was allowed to stand for 20 min. Hydrazine hydrate (5.4 g, 0.1 mol) was added with stirring, an immediate blue precipitate of 3,5-dimethyl-4-nitrosopyrazole resulting. This was filtered off, dried in air and recrystallised from benzene, the product having mp 126–127 °C (lit.,[3] 128 °C), visible absorption ($CHCl_3$) λ_{max} /nm 677 (ε_{max}/dm^3 mol^{-1} cm^{-1} 60); δ_H(200 MHz, $CDCl_3$) 2.60; δ_C(50 MHz, $CDCl_3$) 144.0 (3,5-C), 160.97 (4-C), 11.38 (3,5-CH_3); *m/z* = 125 (M^+, 100), 66 (10.3), 42 (60.3), 41 (10.3); μ = 4.45 D (1 D = 3.336 × 10^{-30} C m).

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Table 1 1,3,5-Trisubstituted-4-nitrosopyrazoles prepared and studied

	1-Substituent	3-Substituent	5-Substituent
1	H	Me	Me
2	H	Bu^t[a]	Me[a]
3	H	Ph[a]	Me[a]
4	Me	Me	Me
5	Ph	Me	Me
6	Me	Bu^t	Bu^t
7	Me	Bu^t[b]	Me[b]
8	Me	Ph[b]	Me[b]
9	Me	Bu^t	Me
10	Me	Me	Bu^t
11	H	Bu^t	Bu^t

[a] Rapid NH tautomerism renders 3 and 5 positions equivalent. [b] 3 and 5 positions may be reversed.

3(5)-Methyl-5(3)-*tert*-butyl-4-nitrosopyrazole (2). This was prepared from reaction of 5,5-dimethylhexane-2,4-dione 3-oxime with hydrazine hydrate. 5,5-Dimethylhexane-2,4-dione was first prepared by the literature method,[19-21] nitrosated as for acetylacetone but using glacial acetic acid in place of hydrochloric acid, and reacted with hydrazine hydrate without further purification, and the product recrystallised as before. 3(5)-Methyl-5(3)-*tert*-butyl-4-nitrosopyrazole (51% yield) [mp 161–163 °C (lit.,[7] 164 °C)]; λ_{max}(CH_3OH)/nm 676 (ε_{max}/dm^3 mol^{-1} cm^{-1} 47); δ_H(60 MHz, $CDCl_3$), 2.27 [3 H, s, 3(5), Me], 1.72 [9 H, s, 5(3) Bu^t]; δ_C(50 MHz, $CDCl_3$), 160.0 (C-Bu^t), 159.46 (C-4), 135.70 (C-Me), 34.07 [$C(CH_3)_3$], 30.17 [C(CH_3)$_3$], 13.13 (CH_3); *m/z* = 167 (M^+, 100), 150 (M^+ − OH, 29.3), 109 (20.7), 82 (17.4).

3(5)-Methyl-5(3)-phenyl-4-nitrosopyrazole (3). 1-Benzoylacetone was nitrosated using glacial acetic acid as solvent and acid and the product 1-benzoylacetone 2-oxime was reacted with hydrazine hydrate in glacial acetic acid. The green product was filtered off, dried and recrystallised twice from alcohol giving 3(5)-methyl-5(3)-phenyl-4-nitrosopyrazole [mp 152–154 °C (lit.,[3] 149–150 decomp.)]; δ_H(200 MHz, C_2D_6CO), 2.3 [3 H, s, 3(5) Me], 7.5 [3 H, m, 5(3) Ph], 8.3 [2 H, m, 5(3) Ph]; δ_C(50 MHz, C_2D_6CO), 160.3 (C-4), 151.4 [C-5(3)], 132.6 [C-3(5)], 131.0 (C-1, Ph), 130.6 (C-4, Ph), 129.8 (C-2,6 Ph), 129.5 (C-3,5 Ph), 12.4 [3(5)-Me]; λ_{max}(C_2H_5OH)/nm 695 (ε_{max}/dm^3 mol^{-1} cm^{-1} 24); *m/z* = 188 (M + 1$^+$, 10.5), 187 (M^+, 100), 128 (10.7), 104 (PhCNH$^+$, 33.6), 103 (PhCN$^+$, 23.0), 77 (Ph$^+$, 10).

1,3,5-Trimethyl-4-nitrosopyrazole (4). The oxime of acetylacetone, prepared as above, was reacted with methylhydrazine. Recrystallisation from chloroform gave blue needles of 1,3,5-trimethyl-4-nitrosopyrazole [mp 80–81.5 °C (lit.,[3] 80–81 °C)]; λ_{max}(C_6H_6)/nm 687; δ_H(200 MHz, $CDCl_3$), 3.66 (3 H, s, N-Me), 2.70 (3 H, s, 5-Me), 2.16 (3 H, s, 3-Me); δ_C(50 MHz, $CDCl_3$) 160.1 (C-4), 152.0 (C-3), 133.1 (C-5), 25.5 (N-Me), 12.6 (3-Me), 9.5 (5-Me); *m/z* 139 (M^+, 100), 67 (11.3), 56 (15.2); μ = 4.39 D.

1-Phenyl-3,5-dimethyl-4-nitrosopyrazole (5). In an analogous manner, phenylhydrazine hydrochloride was reacted with acetylacetone oxime to give an immediate green precipitate which was filtered, dried and recrystallised from absolute alcohol giving 1-phenyl-3,5-dimethyl-4-nitrosopyrazole as a blue–green solid, [mp 94.5–96 °C (lit.,[3] 95.5–96.5 °C)]; λ_{max}(C_2H_5OH)/nm 684; δ_H(200 MHz, CD_3OD) 7.4 (5 H, s, N-Ph), 2.87 (3 H, s, 5-Me), 2.35 (3 H, s, 3-Me); δ_C(50 MHz, CD_3OD) 161.7 (C-4), 138.9 (C-1 Ph), 130.6 (C-3,5 Ph), 130.55 (C-4, Ph), 126.5 (C-2,6 Ph), 12.95 (3-Me), 11.0 (5-Me).

1-Methyl-3,5-di-*tert*-butyl-4-nitrosopyrazole (6). Dipivaloylmethane was nitrosated with pentyl nitrite and hydrochloric acid to give the oxime which was used without further purification, 0.68 g, 3.2 mmol, being added to a solution of methylhydrazine (3.0 ml, 3.2 mmol) in glacial acetic acid (20 ml) and allowed to stand for 2 h at room temp. The acetic acid was neutralised with sodium hydrogencarbonate and the reaction product extracted into diethyl ether. Removal of the solvent left a thick green oil shown by TLC to contain three components. Crystallisation from light petroleum (bp 40–60 °C) gave blue crystals of 1-methyl-3,5-di-*tert*-butyl-4-nitrosopyrazole (80 mg, 11%) mp 109–111 °C, λ_{max}($CHCl_3$)/nm 688.5 (ε_{max}/dm^3 mol^{-1} cm^{-1} 52), δ_H($CDCl_3$), 4.02 (3 H, s, N-CH_3), 1.74 (9 H, s, 5-Bu^t), 1.10 (9 H, s, 3-Bu^t); δ_C(50 MHz, $CDCl_3$), 161.7 (C-4), 160.0 (C-3), 144.5 (C-5), 41.2 (N-CH_3), 35.6 [3-$C(CH_3)_3$], 33.0 [5-$C(CH_3)_3$], 31.7 [3-C(CH_3)$_3$], 27.4 [5-C(CH_3)$_3$]; *m/z* 224 (M^+ + 1, 12.0), 223 (M^+, 100), 206 (M^+ − OH, 10), 150 (17.0), 109 (10.0), 57 ($C_4H_9^+$, 18.0), 42 (10.0).

1,5-Dimethyl-3-*tert*-butyl-4-nitrosopyrazole (7). 5,5-Dimethylhexane-2,4-dione 3-oxime, prepared by nitrosation of the dione, was stirred with a fourfold excess of methylhydrazine in water to give a blue–green oil. This was extracted into diethyl ether, shaken with sodium hydrogencarbonate to neutralise, separated and solvent removed. Column chromatography (silica–toluene) gave a blue oil of 1,5-dimethyl-3-*tert*-butyl-4-nitrosopyrazole. TLC and gas chromatography demonstrated the presence of only one of the two possible isomers, λ_{max}($C_6H_5CH_3$)/nm 701; δ_H(60 MHz, CCl_4), 3.56 (3 H, s, N-CH_3), 2.24 (3 H, s, 5-CH_3), 1.38 (9 H, s, 3-C(CH_3)$_3$; δ_C(50 MHz, $CDCl_3$) 160.25 (C-4), 157.8 (C-3), 133.5 (C-5), 35.1 (N-CH_3), 33.7 [3$C(CH_3)_3$], 29.6 [3-C[CH_3)$_3$], 10.3 (5-CH_3).

1,5-Dimethyl-3-phenyl-4-nitrosopyrazole (8). 1-Benzoylacetone 2-oxime (1 g, 5.2 mmol) was added to a solution of methylhydrazine (0.5 g, 10 mmol) in glacial acetic acid and the resultant dark-green solution was neutralised with sodium hydrogencarbonate. Following diethyl ether extraction and solvent removal, the green solid was recrystallised from chloroform giving 1,5-dimethyl-3-phenyl-4-nitrosopyrazole, mp 96–97 °C; λ_{max}($CHCl_3$)/nm 695 (ε_{max}/dm^3 mol^{-1} cm^{-1} 33); δ_H(200 MHz, $CDCl_3$) 2.35 (3 H, s, 5-CH_3), 3.75 (3 H, s, N-CH_3), 7.45 (3 H, m, 3-Ph), 8.2 (2 H, m, Ph); δ_C(50 MHz, $CDCl_3$) 159.6 (C-4), 149.9 (C3), 130.4 (C-5), 131.1 (C-1, Ph), 129.4 (C-4, Ph), 129.0 (C-2,6 Ph), 128.4 (C-3,5 Ph); *m/z* 201 (M^+, 100), 56 ($CH_3CNCH_3^+$, 42).

1,5-Dimethyl-3-isobutyl- (9) and 1,3-dimethyl-5-isobutyl-4-nitrosopyrazole (10). 6-Methylheptane-2,4-dione was nitrosated in glacial acetic acid and, following standing at room temp. for 1 h, an equimolar quantity of methylhydrazine in water was added resulting in the formation of a blue solution. This was extracted into diethyl ether, separated and neutralised with sodium hydrogencarbonate solution. Removal of the solvent gave a green oil which showed two blue spots on TLC analysis. Gas chromatography indicated the presence of two compounds in the ratio of 1:1. Column chromatography (silica, ether–toluene 1:10) afforded complete separation, giving 1,5-dimethyl-3-isobutyl-4-nitrosopyrazole, blue oil, λ_{max}($C_6H_5CH_3$)/nm 693.5; δ_H(200 MHz, $CDCl_3$), 3.8 (3 H, s, N-CH_3), 2.7 (3 H, s, 5-CH_3), 2.6 (2 H, s, CH_2 3-Bu^i), 1.9 (1 H, s, CH 3-Bu^i), 0.9 (6 H, d, 2CH_3 3-Bu^i); *m/z* 181 (M^+, 64), 164 (M^+ − OH, 100), 123 (M^+ − C_4H_{10}, 43.6), 82 (16.4), 56 (10.7) and 1,3-dimethyl-5-isobutyl-4-nitrosopyrazole, blue oil, λ_{max}($C_6H_5CH_3$)/nm 693.5; δ_H(200 MHz, $CDCl_3$), 3.8 (3 H, s, N-CH_3), 3.1 (2 H, s, CH_2 5-Bu^i), 2.3 (3 H, s, 3-CH_3), 2.2 (1 H, s, CH 5-Bu^i), 1.0 (6 H, d, 2CH_3 5-Bu^i); *m/z* 181 (M^+, 100), 164 (M^+ − OH, 44.2), 124 (M^+ − C_4H_9), 11.2, 123 (80.8), 82 (20.0) and 59 (13.8).

3,5-Di-*tert*-butyl-4-nitrosopyrazole[7] (11). The sample gave δ_C(200 MHz, $CDCl_3$) 161.5 (C-4), 156.5 (C-3,5), 36.0 [3,5-$C(CH_3)_3$], 31.0 [3,5-C(CH_3)$_3$]; *m/z* 210 (M^+ + 1, 12.2), 209 (M^+, 100), 192 (M − OH$^+$, 20.0), 136 (26.1), 82 (17.2), 59 (12.8) and 57 (33.3).

Results

Variable temperature ^{1}H NMR measurements were undertaken for 1,3,5-trimethyl- and 1-phenyl-3,5-dimethyl-4-nitrosopyrazole. At room temperature two sharp signals were observed for the methyl groups at δ 2.87 and 2.36. On lowering the temperature to −60 °C, four signals resulted, namely two intense signals

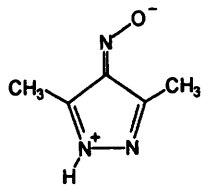
at δ 2.15 and 3.17 with smaller peaks at δ 2.20 and 3.07. These results arise from the presence of two conformers due to the slowing down of the rotation of the NO group, a feature well-documented in the literature for nitrosoarenes, see *e.g.* ref. 22, though noted only infrequently in nitroso heterocycles.[23] Further considerations of these effects, and of the parallel effects in the temperature dependent ^{13}C NMR spectra, together with identification of the conformers, are deferred to later papers in this series.

Discussion of the results

The ^{13}C NMR evidence affords confirmation of the expected marked differences between the five- and six-membered ring systems where the NO group is situated between flanking *tert*-butyl substituent groups. We have shown[15] in the case of the C_6 ring that the SCS for the NO group is enhanced above that for nitrosobenzene itself by 16.5 ppm, and have associated this unusually large increase with the NO group taking up the orthogonal position in the sterically hindered compound.

Comparison with the corresponding 4-nitrosopyrazoles gives the following SCS values: 3,5-dimethyl-4-nitrosopyrazole 56.2 ppm, 3,5-di-*tert*-butyl-4-nitrosopyrazole 64.6 ppm, 1,3,5-trimethyl-4-nitrosopyrazole 54.7 ppm, 1-methyl-3,5-di-*tert*-butyl-4-nitrosopyrazole 62.4 ppm. The enhancement of the SCS values on changing the flanking groups from methyl to *tert*-butyl is thus 8.4 and 7.7 ppm respectively. It therefore appears that any tendency to a sterically fixed orthogonality in the case of these 3,5-di-*tert*-butyl-4-nitrosopyrazoles is far less than in the corresponding more restricted benzene systems. Such a conclusion is in keeping with simple considerations of the geometry of the respective five- and six-membered rings. The SCS values for the NO group in other 4-nitrosopyrazoles are 59.6 ppm (3-methyl-5-*tert*-butyl), 57.4 ppm (3-methyl-5-phenyl), 56.4 ppm (1,5-dimethyl-3-phenyl), and 54.9 ppm[12] (1-methyl-3,5-diphenyl).

The ^{13}C NMR SCS values for 4-substituted pyrazoles can be readily compared with those for substituted benzenes[24,25] (see Table 2). In Fig. 1 we compare the best straight lines for SCS (X) in 1-methyl-4-X, 4-X-, and 3,5-dimethyl-4-X-pyrazoles with the benzene SCS values. When the case of X = NO is omitted the three lines obtained are almost identical, the slopes being in the range 0.74 ± 0.01. Inclusion of the nitroso substituent substantially modifies the slope of the best straight line to 0.695. It is possible that this is due to the participation of the quinonoid canonical form (**1**) when the 4-X-substituent is the powerful π-electron acceptor group NO and that this effect is negligible for other less powerful π-electron acceptors such as the nitro group.



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It is of interest to note that the ^{13}C chemical shifts of the two equivalent methyl groups in both 2,6-dimethyl-X-benzenes and 3,5-dimethyl-4-X-pyrazoles vary according to the character of X. The data are summarised in Table 3. The changes in these chemical shifts are much greater in the case of the substituted benzenes than for the substituted pyrazoles, the major difference being that the chemical shift of the methyl group is increased in the benzene case only for the bromine substituent,

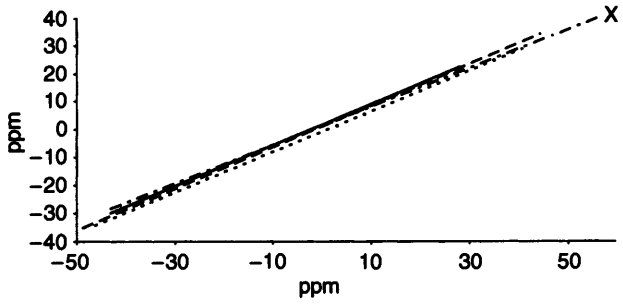

Fig. 1 SCS values (ppm) for 4-substituted pyrazoles (horizontal axis) *vs.* corresponding SCS values (ppm) for phenyl-X (vertical axis). Best straight lines given for 4-X-pyrazole (– – –), 1-methyl-4-X-pyrazole (- - -), 3,5-dimethyl-4-X-pyrazole, (*a*) excluding X = NO (——), (*b*) including X = NO (– – – – –). 3,5-Dimethyl-4-nitrosopyrazole is indicated by X.

Table 2 ^{13}C SCS values for substituents X in PhX and 4-X-pyrazoles relative to X = H[a]

X	PhX	1	2	3	4	5	6
Me	9.3	5.9	5.8	8.5	8.1	10.5	10.5
Ph	13.0			15.1	15.8		20.0
NH_2	20.2	28.1		25.3			25.2
OMe	31.4			35.9			35.9
Cl	6.4	3.1	1.5	3.0	4.4	4.4	4.1
Br	−5.9	−12.3	−11.8	−12.5	−11.5	−14.4	−13.2
I	−32.3	−43.1	−42.2	−46.3			−48.8
CO_2Ft	2.4			4.1			
COOH	2.1		4.9				
COMe	8.9			14.3	15.6		16.1
COPh	0.1			15.5			
CHO	8.2			18.3	12.0	18.3	
Vinyl	9.1			15.4	10.8		
CN	−15.5			−10.7		−14.8	−15.0
NO_2	20.6	26.8	25.9	28.0			29.8
NO	37.6	56.2	54.7				
OH	26.9					35.5	31.4
F	34.8						39.5
CHNPh	8.9				9.7		
CO_2Me	2.1				1.1		

[a] **1** = 3,5-Dimethyl-4-X-pyrazole. **2** = 1,3,5-Trimethyl-4-X-pyrazole. **3** = 1-Methyl-4-X-pyrazole. **4** = 1-Phenyl-4-X-pyrazole. **5** = 1-Benzyl-4-X-pyrazole. **6** = 4-X-Pyrazole. Pyrazole data from ref. 26, phenyl-X data from ref. 25, with the exception of the NO cases from this work for pyrazoles and ref. 24 for PhNO. All values in ppm.

Table 3 Comparison of ^{13}C methyl shifts[a] in 2,6-dimethyl-1-X-benzenes with 3,5-dimethyl-4-X-pyrazoles

X	2,6-Di-Me-1-X-benzene[b]	3,5-Di-Me-4-X-pyrazole[c]
H	21.25	11.9
Br	23.80	10.9
Cl	20.64	10.3
F	14.48	
NH_2	17.40	9.8
NMe_2	19.08	
NHCOMe	18.20	
OH	15.71	
OMe	15.09	
CN	20.51	
COOH	20.10	
COOMe	19.56	
NO_2	17.25	12.7
Bu^t		14.3
Et		10.4
NO	19.04	11.4
I		12.4
COMe	17.80	
NC	18.7	

[a] All values in ppm relative to $SiMe_4$ (δ = 0). [b] $CDCl_3$ solutions, ref. 27 excepting NO,[30] COMe[31] and NC.[32] $(CD_3)_2SO$ solutions, ref. 26.

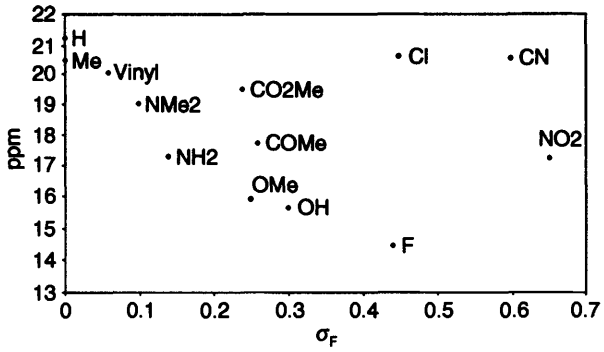

Fig. 2 ^{13}C chemical shift values (ppm) for the methyl substituents in 2,6-dimethyl-X-benzenes (vertical axis) *vs.* σ_F values for X (horizontal axis)

whereas in the pyrazole case this effect occurs for the iodine and nitro substituents. Inspection of the literature shows that these features are repeated for the methyl shifts of 1-X-2-methylbenzenes on the one hand, and 3-methyl-4-X-, 1,3-dimethyl-4-X-, 1,5-dimethyl-4-X- and 1,3,5-trimethyl-4-X-pyrazoles on the other. To the best of our knowledge, little attention has been directed to the correlations between the chemical shifts of the flanking methyl groups and the character of the substituent X in the case of the substituted benzenes. There is a general relationship between the chemical shifts and the following parameters of the groups X, namely i,[28] σ_χ[29] and σ_F.[29] The first two of these are electronegativity substituent parameters of short interaction range, whereas the third is a long range field effect transmitted either through space or through polarisable bonds in the aromatic framework. Inspection of Fig. 2 suggests that, although in most cases the chemical shift diminishes as the substituent constant σ_F increases, there is no single parameter governing the change. In the case of the 3,5-dimethylpyrazoles the methyl groups are situated at a greater distance from the substituents X than in the six-membered ring and the correlation is weaker.

It is noteworthy that the preparative route for 1,3(5)-dimethyl-5(3)-R-4-nitrosopyrazoles leads to two products in virtually equal proportions when R = Bu^i, but that only one product is detected when R = Bu^t or Ph, suggesting that steric factors may be responsible for the production of the single isomer. Further, more detailed, studies are necessary to confirm this provisional hypothesis.

The mass spectral data were all obtained at a low electron accelerating potential of 15 eV. Comparison of the mass spectra of 3,5-dimethylpyrazole obtained at both 15 and 70 eV indicates that at 15 eV the mass spectrum is simpler due presumably to the absence of fragmentation of the pyrazole ring for which the appearance potentials are larger than 15 eV. All of the nitrosopyrazoles studied give no $M^+ - 30$ peak. This contrasts with the case for many nitrosobenzene derivatives. On the other hand, when an isobutyl or *tert*-butyl group is present in the 3 or 5 position the $M^+ - 17$ peak is observed, implying OH elimination from the molecular ion. The absence of such peaks for the case of methyl or phenyl groups in the 3 or 5 positions is noted and it would be worthwhile to investigate the mass spectra of other 4-nitrosopyrazoles containing alkyl groups larger than methyl in the 3 or 5 positions.

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