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EPR Studies of 1-Methyl-2-substituted-5-pyrrolylcarbonyl Fluorinated Nitroxides and Dual-parameter Correlation Analysis of Their Hyperfine Splitting Constants

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Abstract: Three series of new 1-methyl-2-substituted-5-pyrrolylcarbonyl fluorinated nitroxides, i.e., **3** ($R_f = C_2F_5$), **4** ($R_f = n\text{-}C_3F_7$) and **5** ($R_f = n\text{-}C_7F_{15}$), generated by the H-abstraction/spin-trapping reaction of eleven 1-methyl-2-substituted-pyrrole-5-carbaldehydes (**6**) with the H-abstracting agent [$R_fN(O^\bullet)R_f$] **1** and the spin-trapping agent R_fNO **2**, were studied by EPR. Correlation analysis of their a_N values with polar and spin-delocalization substituent constants shows that a_N values are mainly affected by the polar effect of the 2-substituent, but the spin-delocalization effect also exists.

Introduction

Largely because nitroxides often exhibit a chemical inertness quite different from most other unstable free radicals, nitroxides continue to be the subject of intensive investigation both from the theoretical and applied viewpoints. The simple diakyl nitroxides $RN(O^\bullet)R$, with α-hydrogen on the carbon adjacent to the nitrogen, typically undergo disproportionation reactions producing nitrones and *N*-hydroxyamines.[1, 2] In contrast to the hardly isolable dialkyl nitroxides bearing β-hydrogen, $CF_3N(O^\bullet)CF_3$, known since 1965, is a stable and isolable compound.[3] Rather surprisingly, $CF_3N(O^\bullet)CF_3$ was the only nitroxide of the bis(perfluoroalkyl) type which had been studied in detail[4] until the development of our novel and general method for the generation of reagents of this type in 1986 by the spontaneous electron transfer initiated reactions between per(poly)fluorodiacyl peroxides $(R_fCO_2)_2$ and carbanions derived from nitroalkanes. Since then, a large number of fluorinated nitroxides with a wide variety of structures have been generated in various new electron transfer reaction systems.[5]

Notably, we have developed a novel and unique technique of spin-trapping termed "*in situ* spin trapping". This technique has proved to be extremely useful for mechanistic studies of electron transfer reactions by EPR spectroscopy and for the synthesis of numerous fluorinated nitroxides. The blue F113 ($CClF_2\text{-}CCl_2F$) solutions containing both the very effective H-abstracting agents, bis-per(poly)fluoroalkyl nitroxides $R_fN(O^\bullet)R_f$ **1** and the fluorinated nitrosoalkanes R_fNO **2** as spin traps, could be simultaneously generated by the reactions of $(R_fCO_2)_2$ with $NaNO_2$.[6] They were used in the study of H-abstraction from many kinds of substrates such as alkanes[7],

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aldehydes[8], ethers[9], alcohols[10], 2-aminopyrimidines[11] and silicones[12]. In these reactions, the radical intermediates generated by the H-abstraction were immediately trapped by R_fNO. From the well-resolved EPR spectra of the spin adducts, a large number of fluorinated nitroxides have been identified and much valuable information about hyperfine splitting constants (hfsc), e.g., a_N, a_F^{β}, a_H^{β} and a_F^{γ} values, substituent effects, temperature dependence of hfsc, as well as selective line broadening has been obtained.[13]

It has been reported many a time that EPR a_N values of nitroxides can be correlated with Hammett-type polar substituent constants σ^x by the single-parameter eqn. (2).[14] However, our recent correlation analysis results for the a_N values of bis(*p*-substituted)phenyl nitroxides[15] and *p*-substituted benzoyl *tert*-butyl nitroxides[16] have shown that, if a sufficient number of well distributed substituents are used, then application of the dual-parameter eqn. (1), in which $\sigma^{\bullet}$ stands for the spin-delocalization substituent constant, together with a closer examination of the experimental data, may reveal an independent spin-delocalizing effect of the substituent Y.

$$\text{variable} = \rho\,\sigma_x + \rho^{\bullet}\sigma^{\bullet} + C \qquad (1)$$

$$\text{variable} = \rho\,\sigma_x + C \qquad (2)$$

$$\text{variable} = \rho^{\bullet}\sigma^{\bullet} + C \qquad (3)$$

On the basis of our studies,[17(a),(b) and (c)] we came to realize that the $|\rho_{mb}/\rho_{JJ}^{\bullet}|$ ratio may serve as a rough measure of the relative importance of the polar and the spin-delocalization effects of substituents, and four categories of possible circumstances might be visualized in the absence of measurable steric effects: **I**. When both polar and spin effects are important, the $|\rho_{mb}/\rho_{JJ}^{\bullet}|$ values might fall in the range of (very) roughly 0.2 – 0.8. Under these circumstances, the necessity of using the dual-parameter eqn. (1) can be easily established because it yields much better correlation results than those from eqn.(2). Correlation results of the fluorescence spectral data of substituted styrenes and α-methylstyrenes[18] have been found to fall in this category. **II**. When polar effects dominate, this ratio might be around or greater than unity, e.g., in H-atom abstraction reactions by electrophilic radicals,[19] addition reactions to phenylacetylenes by electrophilic radicals,[20] and EPR data of some phenylnitroxides.[15,16] Under these circumstances, using eqn.(1) instead of eqn.(2) may not much improve the correlation results, and the necessity of applying eqn.(1) cannot be established in a definitive manner. However, the existence of the spin effect can still be revealed by careful examination of the individual and total deviations of the experimental data from the regression lines of eqn.(1) and eqn.(2). **III**. When the spin-delocalization effect dominates, then eqn.(3) easily applies, and the use of eqn.(1) may not much improve the correlation results. Application of eqn.(1) might yield a $|\rho_{mb}/\rho_{JJ}^{\bullet}|$ ratio of less than 0.2. A small $|\rho_{mb}/\rho_{JJ}^{\bullet}|$ value suggests the dominance of the spin effect, but it does not necessarily signify the absence of the polar effect. **IV**. When there are other complicating and interacting factors, then none of the three equations can be successfully applied.[21]

The substrates chosen for our former correlation analysis were phenyl derivatives. However, there is no report about the correlation analysis by the dual-parameter eqn. (1) of the EPR data of heterocyclic aromatic fluorinated nitroxides. In consideration of the higher degree of polarization of the 1-methylpyrrolyl derivatives than the corresponding phenyl derivatives, we would like to know if the correlation analysis of EPR data of 1-methyl-2-substituted-5-pyrrolylcarbonyl fluorinated nitroxides **3** ($R_f = C_2F_5$), **4** (R_f = *n*-C_3F_7) and **5** (R_f = *n*-C_7F_{15})

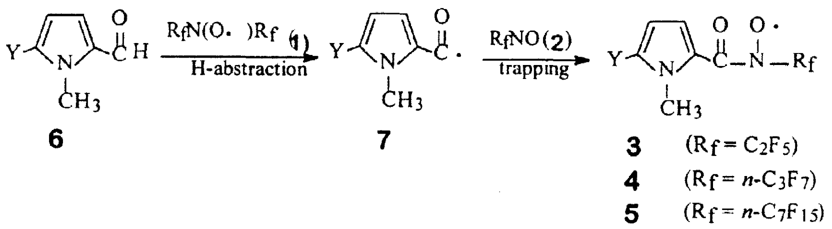
conform to any one of the Category-**I**, Category-**II** or Category-**III** behavior. In this paper, we report EPR studies of these new fluorinated nitroxides **3**, **4** and **5**, generated by the novel H-abstraction/spin-trapping reaction of 1-methyl-2-substituted-pyrrole-5-carbaldehydes (**6**) and the correlation analysis of their a_N values.

Results and discussion

When **6** was mixed with bisperfluoroalkyl nitroxides **1** and fluorinated nitrosoalkanes **2** at room temperature, the hydrogen of the formyl group was easily abstracted by the very effective H-abstracting agent **1** to produce 1-methyl-2-substituted-5-carbonyl radical 7. This radical intermediate 7 was then immediately trapped by the nitroso spin trap **2** to form **3**, **4** or **5**, as depicted in Scheme 1.

The typical EPR spectrum of fluorinated nitroxide, e.g., **3**(Y=CN) and **4**(Y=$COCH_3$), was shown in Fig. 1. From the well-resolved EPR spectra, g values and hfsc, i.e., a_N, a_F^{β}, and a_F^{γ} values were measured and summarized in Table 1 (for **3**), Table 2 (for **4**) and Table 3 (for **5**).

Scheme 1



Y = H, CH_3, Cl, CN, $COCH_3$, NO_2, SCH_3, $COOCH_3$, $Si(CH_3)_3$, Br, OCH_3

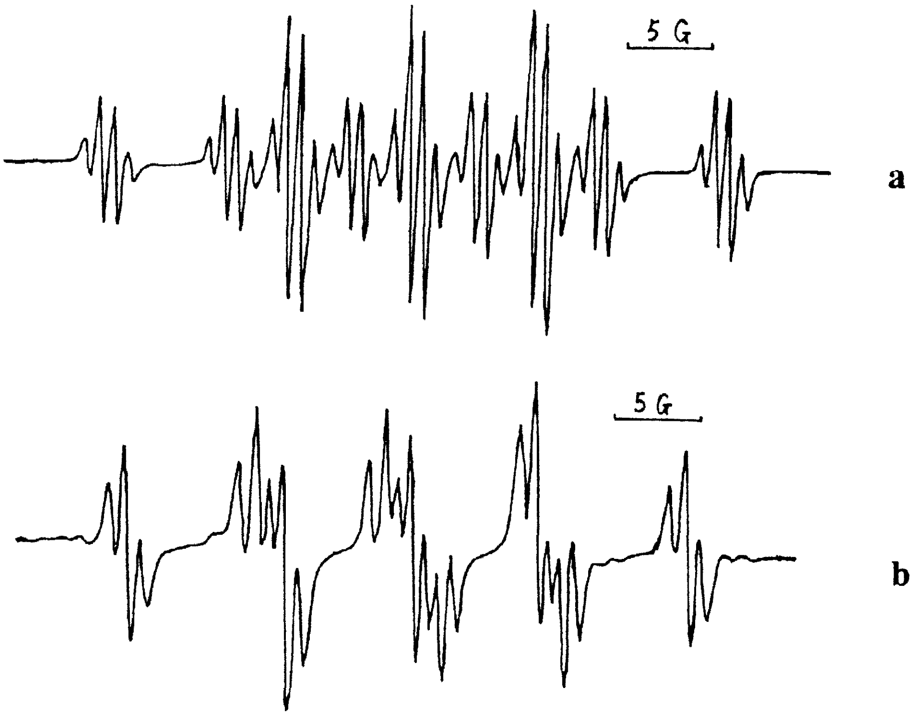


Fig. 1 Typical EPR spectrum for fluorinated nitroxide **3**(Y=CN) (**a**) and **4**(Y=$COCH_3$) (**b**)

Table 1. EPR parameters of fluorinated pyrrolyl nitroxides **3** ($R_f = C_2F_5$) generated by the reactions of **6** with [$C_2F_5N(O^\bullet)C_2F_5 + C_2F_5NO$] in F113 at room temperature (hfsc ± 0.05G)

Y	g	a_N (G)	a_F^β (G)	a_F^γ (3F, G)
H	2.0062	7.95	11.98	0.88
CH_3 [a]	2.0063	8.28	12.20	0.94
Cl	2.0063	8.02	12.18	0.89
CN	2.0063	7.34	11.19	0.87
$COCH_3$	2.0062	7.58	11.58	0.81
NO_2	2.0062	7.26	10.91	0.79
COOH [b]	—	—	—	—
SCH_3	2.0062	8.44	12.78	0.96
$COOCH_3$	2.0063	7.63	11.73	0.85
$Si(CH_3)_3$	2.0062	8.10	12.16	0.88
Br	2.0062	8.04	12.21	0.90
OCH_3	2.0063	8.75	12.90	0.98

a. In addition to **3**(R_F=C_2F_5), the $OHCC_4H_2N(CH_3)CH_2N(O^\bullet)C_2F_5$ nitroxide, with g = 2.0063, a_N = 11.85, a_F^β = 15.08, a_H^β = 8.20, a_F^γ = 0.89 G was also found as a minor product.

b. Only $C_2F_5N(O^\bullet)C_2F_5$ spectrum was obtained because of low solubility of **6**(Y=COOH) in CH_2Cl_2.

Table 2. EPR parameters of fluorinated pyrrolyl nitroxides **4** (R_f = *n*-C_3F_7) generated by the reactions of **6** with [$C_3F_7N(O^\bullet)C_3F_7$ + *n*-C_3F_7NO] in F113 at room temperature (hfsc ± 0.05G)

Y	g	a_N (G)	a_F^β (G)	a_F^γ (2F, G)
H	2.0062	7.80	9.80	0.88
CH_3 [a]	2.0063	8.08	9.88	0.95
Cl	2.0063	7.89	9.97	0.91
CN	2.0063	7.33	8.95	0.80
$COCH_3$	2.0062	7.48	9.60	0.82
NO_2	2.0063	7.21	8.79	0.77
SCH_3	2.0062	8.21	10.14	1.01
$COOCH_3$	2.0063	7.58	9.47	0.80
$Si(CH_3)_3$	2.0062	7.97	9.89	0.86
Br	2.0062	7.93	9.95	0.89
OCH_3	2.0062	8.50	10.98	1.05

a. In addition to **4**(R_F=n-C_3F_7), the $OHCC_4H_2N(CH_3)CH_2N(O^\bullet)C_3F_7$ nitroxide, with g = 2.0063, a_N = 11.30, a_F^β = 14.17, a_H^β = 8.01, a_F^γ = 1.40 G was also found as a minor product.

Table 3. EPR parameters of fluorinated pyrrolyl nitroxides **5** (R_f = *n*-C_7F_{15}) generated by the reactions of **6** with [$C_7F_{15}N(O^\bullet)C_7F_{15}$ + *n*-$C_7F_{15}NO$] in F113 at room temperature (hfsc ± 0.05G)

Y	g	a_N (G)	a_F^β (G)	a_F^γ (2F, G)
H	2.0062	7.82	9.81	0.89
CH_3 [a]	2.0063	8.05	9.85	0.93
Cl	2.0062	7.88	9.95	0.92
CN	2.0062	7.31	8.92	0.82
$COCH_3$	2.0063	7.49	9.64	0.82
NO_2	2.0062	7.21	8.80	0.77
SCH_3	2.0062	8.18	10.10	1.02
$COOCH_3$	2.0063	7.60	9.46	0.84
$Si(CH_3)_3$	2.0062	7.95	9.90	0.85
Br	2.0063	7.89	9.94	0.89
OCH_3	2.0063	8.45	10.96	1.06

a. In addition to **5**(R_F=n-C_7F_{15}), the $OHCC_4H_2N(CH_3)CH_2N(O^\bullet)C_7F_{15}$ nitroxide, with g = 2.0063, a_N = 11.28, a_F^β = 14.10, a_H^β= 8.05, a_F^γ = 1.42 G was also found as a minor product.

Tables 1, 2 and 3 show that an electron-pair acceptor group, e.g., CN, $COCH_3$, NO_2 and $COOCH_3$, decreases the a_N value, while a donor, e.g., $Si(CH_3)_3$ and OCH_3, increases the a_N value. It has been found experimentally that when an electron-pair acceptor is attached to the pyrrole ring, the H-abstraction and spin-trap rates are moderate and the final fluorinated nitroxide could last 8 - 12 h. However, when a donor is attached to the pyrrole ring, the H-abstraction and spin-trap rates are very fast and the final fluorinated nitroxide could only last 0.5 - 2 h.

Tables 1, 2 and 3 also show that a_N values of **3** (R_f = C_2F_5) are larger than those of **4** (R_f = *n*-C_3F_7) and **5** (R_f = *n*-C_7F_{15}). Possibly, this might be a reflection of the fact that the electron-pair attracting power of perfluoroalkyl groups *n*-C_3F_7 and *n*-C_7F_{15} is larger than that of C_2F_5,[5b, 22] because greater electron-pair attraction disfavors the resonance structure with the spin together with a positive charge on the nitrogen atom.

Values of representative Hammett-type unresolved polar substituent constants (σ_x), i.e., σ_p, σ^+ and σ_{mb}, were taken from ref. 23, 23 and 24 respectively. Values of representative spin-delocalization constants ($\sigma^\bullet$), i.e., $\sigma_{JJ}^\bullet$, $\sigma_c^\bullet$, $\sigma_\alpha^\bullet$, were taken from ref. 24, 25 and 26 respectively. Results of correlation analysis in terms of ρ, $\rho^\bullet$, s, r or R, ψ and F values by eqn. (1)-(3) are summarized in Table 4 (for **3**), 5 (for **4**) and 6 (for **5**).[27] The identity of the substituents used in each entry is given in the footnotes of the tables. As mentioned previously, a confidence level (CL) above 99.9% (based on $F_{0.001}$ values given in the footnotes of the tables; *cf.* Ref. 21a and 21b) is considered good, even though the r (or R) value is smaller than 0.95, because the r value does not take into account the number of substituents (n).

Table 4 Values of ρ and $\rho^{\bullet}$ of eqn. (1), (2) and (3), and the corresponding values of the correlation coefficient r or R, ψ, s and F-test for correlation of a_N values of **3** ($R_f = C_2F_5$) with σ_x and $\sigma^{\bullet}$

σ_x or $\sigma^{\bullet}$ or ($\sigma_x + \sigma^{\bullet}$)	ρ	$\rho^{\bullet}$	r or R	s	ψ	F [a]	n[b]
σ_p	- 1.241		0.9397	0.1657	0.3781	67.94	11
σ^+	- 0.8928		0.9806	0.0971	0.2190	200.6	10
σ_{mb}	- 0.9082		0.9789	0.0990	0.2259	206.6	11
$\sigma_p + \sigma_{JJ}^{\bullet}$	- 1.345	0.5171	0.9569	0.1493	0.3407	43.37	11
$\sigma^+ + \sigma_{JJ}^{\bullet}$	- 0.8899	- 0.1823	0.9827	0.0980	0.2209	98.93	10
$\sigma_{mb} + \sigma_{JJ}^{\bullet}$	- 0.9589	0.4036	0.9894	0.0746	0.1703	185.7	11
$\sigma_p + 10\,\sigma_{\alpha}^{\bullet}$	- 1.450	0.5175	0.9517	0.1583	0.3761	28.81	9
$\sigma^+ + 10\,\sigma_{\alpha}^{\bullet}$	- 0.8759	- 0.1793	0.9857	0.0887	0.2130	85.64	8
$\sigma_{mb} + 10\,\sigma_{\alpha}^{\bullet}$	- 0.9330	0.2577	0.9817	0.0981	0.2330	79.88	9
$\sigma_p + \sigma_c^{\bullet}$	- 1.450	0.6080	0.9520	0.1621	0.3656	33.90	10
$\sigma^+ + \sigma_c^{\bullet}$	- 0.8519	- 0.2808	0.9859	0.0888	0.2003	121.1	10
$\sigma_{mb} + \sigma_c^{\bullet}$	- 0.9484	0.2078	0.9797	0.1062	0.2394	83.72	10

a: Critical F values: $F_{0.001}$ (1, 9) = 22.86; $F_{0.001}$ (1, 8) = 25.42; $F_{0.001}$ (2, 8) = 18.49; $F_{0.001}$ (2, 7) = 21.69; $F_{0.001}$ (2, 6) = 27.00; $F_{0.001}$ (2, 5) = 37.12. b: n = 11, **Y = H, CH_3, Cl, CN, $COCH_3$, NO_2, SCH_3, $COOCH_3$, $Si(CH_3)_3$, Br, OCH_3**; n = 10, all of 11 substituted groups except for **$COCH_3$**; n = 9, all of 11 substituted groups except for **NO_2** and **Br**; n = 8, all of 11 substituted groups except for **$COCH_3$**, **NO_2** and **Br**.

Table 5 Values of ρ and $\rho^{\bullet}$ of eqn. (1), (2) and (3), and the corresponding values of the correlation coefficient r or R, ψ, s and F-test for correlation of a_N values of **4** ($R_f = n\text{-}C_3F_7$) with σ_x and $\sigma^{\bullet}$

σ_x or $\sigma^{\bullet}$ or ($\sigma_x + \sigma^{\bullet}$)	ρ^x	$\rho^{\bullet}$	r or R	s	ψ	F [a]	n[b]
σ_p	- 1.045		0.9367	0.1433	0.3872	64.39	11
σ^+	- 0.7408		0.9701	0.1009	0.2714	127.7	10
σ_{mb}	- 0.7627		0.9730	0.0945	0.2552	159.8	11
$\sigma_p + \sigma_{JJ}^{\bullet}$	- 1.128	0.4083	0.9517	0.1332	0.3599	38.45	11
$\sigma^+ + \sigma_{JJ}^{\bullet}$	- 0.7383	- 0.1534	0.9723	0.1039	0.2796	60.46	10
$\sigma_{mb} + \sigma_{JJ}^{\bullet}$	- 0.8018	0.3114	0.9818	0.08244	0.2227	106.9	11
$\sigma_p + 10\,\sigma_{\alpha}^{\bullet}$	- 1.187	0.3930	0.9440	0.1412	0.4041	28.56	9
$\sigma^+ + 10\,\sigma_{\alpha}^{\bullet}$	- 0.7102	- 0.1444	0.9774	0.09114	0.2677	53.33	8
$\sigma_{mb} + 10\,\sigma_{\alpha}^{\bullet}$	- 0.7652	0.1816	0.9752	0.0948	0.2713	58.15	9
$\sigma_p + \sigma_c^{\bullet}$	- 1.195	0.4607	0.9453	0.1450	0.3899	29.39	10
$\sigma^+ + \sigma_c^{\bullet}$	- 0.7011	- 0.2729	0.9772	0.0944	0.2539	74.03	10
$\sigma_{mb} + \sigma_c^{\bullet}$	- 0.7820	0.1315	0.9726	0.1033	0.2778	61.27	10

Note a. and b. are the same as that in Table 4.

Table 6 Values of ρ and $\rho^\bullet$ of eqn. (1), (2) and (3), and the corresponding values of the correlation coefficient r or R, ψ, s and F-test for correlation of a_N values of **5** ($R_f = n\text{-}C_7F_{15}$) with σ_x and $\sigma^\bullet$

σ_x or $\sigma^\bullet$ or ($\sigma_x + \sigma^\bullet$)	ρ^x	$\rho^\bullet$	r or R	s	ψ	F^a	n^b
σ_p	- 1.011		0.9433	0.1305	0.3670	72.65	11
σ^+	- 0.7139		0.9703	0.0969	0.2704	128.8	10
σ_{mb}	- 0.7352		0.9763	0.0850	0.2391	183.4	11
$\sigma_p + \sigma_{JJ}^\bullet$	- 1.085	0.3677	0.9564	0.1217	0.3424	42.92	11
$\sigma^+ + \sigma_{JJ}^\bullet$	- 0.7108	- 0.1901	0.9739	0.0972	0.2713	64.45	10
$\sigma_{mb} + \sigma_{JJ}^\bullet$	- 0.7693	0.2720	0.9836	0.0752	0.2115	118.9	11
$\sigma_p + 10\ \sigma_\alpha^\bullet$	- 1.134	0.3594	0.9475	0.1308	0.3916	28.34	9
$\sigma^+ + 10\ \sigma_\alpha^\bullet$	- 0.6779	- 0.1651	0.9764	0.0890	0.2729	51.19	8
$\sigma_{mb} + 10\ \sigma_\alpha^\bullet$	- 0.7307	0.1571	0.9780	0.0853	0.2554	65.97	9
$\sigma_p + \sigma_c^\bullet$	- 1.143	0.3978	0.9497	0.1341	0.3742	32.21	10
$\sigma^+ + \sigma_c^\bullet$	- 0.6695	- 0.3051	0.9798	0.0855	0.2388	84.21	10
$\sigma_{mb} + \sigma_c^\bullet$	- 0.7465	0.0808	0.9752	0.0947	0.2643	68.05	10

Note a. and b. are the same as that in Table 4.

Single-parameter correlation results for **3** summarized in Table 4 show that correlations with CL's greater than 99.9% can be achieved by eqn. (2) with σ_p, σ^+ or σ_{mb}, i.e., for σ_p: r = 0.9397, Ψ = 0.3781, F = 67.94, n = 11; for σ^+: r = 0.9806, Ψ = 0.2190, F = 200.6, n = 10; for σ_{mb}: r = 0.9789, Ψ = 0.2259, F = 206.6, n = 11. However, single-parameter correlation analyses with all the $\sigma^\bullet$ yield meaningless results (r < 0.55). By using the dual-parameter eqn. (1), all the nine parings of (σ_x, $\sigma^\bullet$) yield good correlations with CL > 99.9%, e.g., for (σ_p, $\sigma_{JJ}^\bullet$): R = 0.9569, ψ = 0.3407, F = 43.37, n = 11; for (σ_{mb}, $\sigma_{JJ}^\bullet$): R = 0.9894, ψ = 0.1703, F = 185.7, n = 11; for (σ^+, $\sigma_c^\bullet$): R = 0.9859, ψ = 0.2003, F = 121.1, n = 10.

Although application of the dual-parameter eqn.(1) seems to improve the correlation results, this improvement cannot be considered meaningful unless we look into our data more closely. It would be good practice to examine the individual deviations (D-1, D-2) as well as the sum of the deviations ($\Sigma|D|$), in which D-1 represents the individual deviation of a_N value from the regression line of the plot of a_N vs. σ_{mb} and D-2 represents the individual deviation of a_N value from the regression line of the plot of a_N vs. ($\rho_{mb}\sigma_{mb} + \rho_{JJ}^\bullet\sigma_{JJ}^\bullet$). Notably, the D-1 of SCH_3 and $Si(CH_3)_3$, which have very weak polar effect but very strong or moderately strong spin-delocalization effects, is 0.18 and 0.13 respectively, but the D-2 of SCH_3 and $Si(CH_3)_3$ is 0.03 and 0.04 respectively. Furthemore, the $\Sigma|D\text{-}2|$ value (0.49) is much smaller than the $\Sigma|D\text{-}1|$ value (0.82). Therefore, we believe that the above-mentioned indecisive improvement by application of the dual-parameter equation is genuine and that the spin-delocalization effect is in operation even though it is overshadowed by the polar effect. Judging by the $|\rho_{mb}/\rho_{JJ}^\bullet|$ value of 2.38 and by careful examination of the individual and total deviations of the experimental data from the regression lines, the behavior of a_N values of **3** can be classified as category-**II**, i.e.,

a_N values of **3** are mainly affected by the polar effects of the substituents, but spin-delocalization effects also exist.

Similar correlation results have been obtained for **4** and **5** (*cf.* Tables 5, 6 and Fig. 2). Therefore, the behavior of a_N values of **4** and **5** can also be classified as category-**II**.

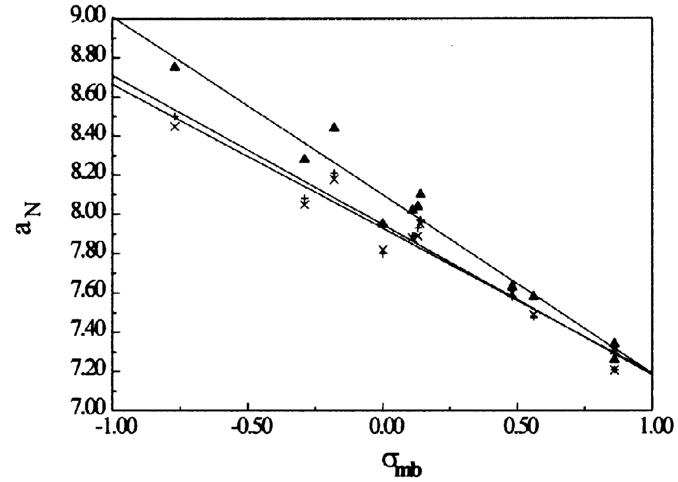
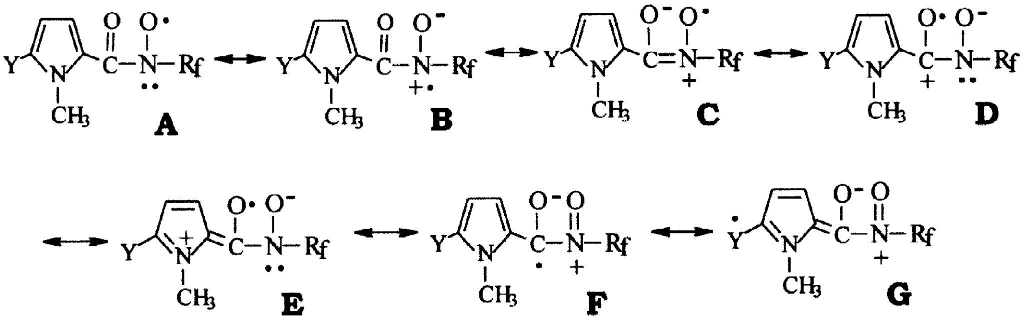


Fig. 2 Plots of a_N values of **3** (▲), **4** (+) and **5** (×) vs. σ_{mb}

It should be noted that all the ρ values derived from the (σ_x, $\sigma^{\bullet}$) combinations are negative, this shows that an electron-pair acceptor will decrease the a_N value, while an electron-pair donor will increase the a_N value. This observation might be simplistically rationalized by the following proposition. Since among the various conceivable resonance structures (**A**-**G**), **B** is the only structure with a spin on the nitrogen atom, polar effects of the Y substituents on the spin density of nitrogen might be understood in terms of their effects on the relative importance of **B**. Evidently, electron-pair donors would favor **B**, while acceptors would disfavor it. In other words, donors should increase the a_N values, while acceptors should decrease them. Furthermore, the relative unimportance of the spin-effects of Y substituents might be conceived as a consequence of the relative unimportance of the various possible structures of **G**, which depend on the nature of Y.



Experimental

The preparation and characterization of twelve 1-methyl-2-substituted-pyrrole-5-carbaldehydes (**6**) were reported elsewhere.[28] Perfluorodiacyl peroxides $(R_fCO_2)_2$ were prepared from R_fCOCl with H_2O_2 and 12% NaOH in F113 at -8 to -10 °C according to the reported procedure.[29]

Blue F113 solution containing $[R_fN(O^{\bullet})R_f$ and $R_fNO]$ was made before use by mixing F113 solution of $(R_fCO_2)_2$ and dry $NaNO_2$ in a deoxygenated tube with vigorous shaking for about 10 min at room temperature.[6]

In a typical experiment, **6** (*ca.* 20 mg) and dry CH_2Cl_2 (0.2 mL) were added into a deoxygenated EPR tube containing *ca.* 0.2 mL of blue F113 solution $[R_fN(O^{\bullet})R_f$ and $R_fNO]$. The tube was shaken vigorously for several mins, then inserted into an EPR cavity and the EPR spectra of fluorinated nitroxide(s) were recorded immediately.

EPR spectra were recorded by using a Varian E-112 EPR spectrometer at room temperature. The conditions employed were as follows: modulation, 100 KHz; frequency, 9.17 GHz; microwave power, 5 ~ 10 mW; time constant, 0.064 s; sweep width, 100 G; sweep time, 8 min. The magnetic field was determined by an ^{1}H-NMR fieldmeter and the microwave frequency by a superhigh frequencymeter.

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27. As described in tables 4, 5 and 6, r and R are basically of similar nature; the former is the correlation coefficient for simple regression, and the latter is the multiple correlation coefficient for multiple regression, e.g., a dual-parameter correlation. The ψ value is a measure of the goodness of fit which take into account the number of substituents for correlation analysis of substituent effects. A smaller ψ value signifies a better fit. From the F value, i.e., the F-test value, the conficence level (CL) of a correlation analysis can be assessed (see, e.g., Box, G. E.; Hunter, W. G.; Hunder, J. S. *Statistics for Experimenters. An Introduction to Design, Data Analysis and Model Building*, John Wiley: New York, 1978).

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