Electron Delocalisation and Stabilisation in Substituted Amino- and Hydroxypropynyl Radicals

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A series of aminopropynes, $RC{\equiv}CCH_2NH_2$ (R = H, Me, Bu^t, Me_3Si), $RC{\equiv}CCH_2N(SiMe_3)_2$, and hydroxypropynes $RC{\equiv}CCH_2OH$ (R = H, Me, Bu^t, Me_3Si, CF_3, and EtO_2C), were prepared and the corresponding α-aminopropynyl and α-hydroxypropynyl radicals were examined by e.s.r. spectroscopy. For the first series, the C–N bond rotation barriers were determined from the exchange broadening in the spectra and hence radical stabilisation energies were estimated. The spin distribution in these series indicated an extra delocalisation in radicals with captodative substitution.

Mass spectrometric [1], e.s.r.[2–4] and other studies [5,6] have shown that α-aminoalkyl radicals, $R\dot{C}HNH_2$, have a high degree of electron delocalisation onto nitrogen and correspondingly high stabilisation energies (SEs). This type of radical is formed from amino acids [7–9], polypeptides, and related compounds. The e.s.r. spectra of aminopropynyl radicals (**2a**) showed exchange broadening in the accessible temperature range from which the barrier to rotation about the C–N bond was determined.[2] The C–N bond rotation barrier gives a measure of the stabilisation in this type of radical and can be converted into the radical SE when the thermodynamic stabilisation of the propynyl unit is known.[10] We planned to use this characteristic of aminopropynyl radicals in the determination of the C–N rotation barriers and SEs for a range of substituents including captodative types.

$$\underset{(1)}{H_2NCH_2C{\equiv}CR} \longrightarrow \underset{(2)}{H_2N\dot{C}HC{\equiv}CR}$$

a; R = H **b**; R = Me
c; R = Bu^t **d**; R = Me_3Si
e; R = CO_2Et **f**; R = Cl

In particular, when R is an electron-withdrawing substituent, radicals (**2**) have NH_2 as a donor substituent together with a potential acceptor substituent at the radical centre, although the influence of the latter is attenuated by the triple bond. Following the original proposal that captodative substitution would lead to stabilisation in radicals [11] this effect has been suggested by several other groups of workers,[12–14] though under different names. Viehe and his co-workers have explained a variety of phenomena in terms of captodative stabilisation [15–18] but attempts to quantify the thermodynamic stabilisation due to captodative substitution have been rather unsuccessful. Kinetic studies of the addition of alkyl radicals to captodative substitued alkenes gave rather ambiguous results.[19] Thermochemical studies on the decomposition of 2,3-dimethoxy-2,3-diphenylbutane-1,4-dinitrile by Ruchardt and his co-workers failed to find any captodative effect.[20]

In addition, we report our results for substituted hydroxypropynyl radicals (**4**) generated from the corresponding hydroxypropynes (**3**).

$$\underset{(3)}{HOCH_2C{\equiv}CR} \longrightarrow \underset{(4)}{HO\dot{C}HC{\equiv}CR}$$

a; R = H **b**; R = Me
c; R = Bu^t **d**; R = Me_3Si
e; R = CF_3 **f**; R = EtO_2C

By choosing R to be an electron-withdrawing substituent radicals (**4**) become captodative species with OH as the donor group.

Results and Discussion

Synthesis of Aminopropynes and Hydroxypropynes.—Radicals were generated for e.s.r. study by hydrogen abstraction from the corresponding amine or alcohol using photochemically produced t-butoxyl radicals. The propynylic amines (**1b** and **c**) were made from but-2-yn-1-ol and 3,3-dimethylpropyne respectively, by literature methods (see Experimental section). The trimethylsilyl-, ethoxycarbonyl-, and chloro-amines were made from *N*,*N*-bis(trimethylsilyl)propynylamine [21] (**5**) according to the method of Scheme 1.

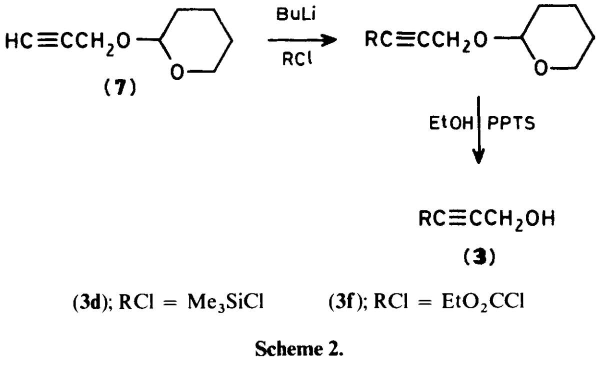
$$\underset{(5)}{HC{\equiv}CCH_2N(SiMe_3)_2} \xrightarrow[RCl]{BuLi} \underset{(6)}{RC{\equiv}CCH_2N(SiMe_3)_2} \xrightarrow[NH_3]{HCl-Et_2O} \underset{(1)}{RC{\equiv}CCH_2NH_2}$$

b; R = Me
d; RCl = Me_3SiCl **e**; RCl = EtO_2CCl
f; R = Cl(RCl = *N*-Chlorosuccinimide)

Scheme 1.

Hydrogen abstraction from *N*,*N*-bis(trimethylsilyl)propynyl amines (**6**) also took place predominantly at the C-atom adjacent to nitrogen and the resulting radicals were studied by e.s.r. spectroscopy.

The acetylenic alcohols (**3d** and **f**) were made from the tetrahydropyranyl (THP) ethers by the method [22] outlined in Scheme 2, where PPTS is pyridinium toluene-*p*-sulphonate.



(**3d**); RCl = Me_3SiCl (**3f**); RCl = EtO_2CCl

Scheme 2.

4,4,4-Trifluorobut-2-yn-1-ol, (**3e**), was made by treatment of 3,3,3-trifluoropropyne with n-butyl-lithium followed by paraformaldehyde. Attempts to prepare methoxy-substituted acetylenes, *i.e.* (**1**; R = OMe) and (**3**; R = OMe) from methoxyacetylene, and otherwise, were unsuccessful.

E.s.r. Spectra of Substituted Aminopropynyl Radicals.—E.s.r. spectra were recorded during irradiation of solutions of the

Table 1. E.s.r. parameters of substituted aminopropynyl radicals $RC{\equiv}C\dot{C}H_{\alpha}NH_2$

Radical	T/K	H.f.s./G $a(H_{\alpha})$	a(N)	$a(NH_2)$	a(other)
(**2a**) R = H^{a}	340	14.7	5.2	1.2	8.1 (1 H)
(**2b**) R = Me	335	15.5	5.0	2.3^{b}	10.3 (3 H)
(**2c**) R = Bu^{t}	340	15.8	5.1	2.3^{c}	0.4 (9 H)
(**2d**) R = Me$_3$Si	340	14.3	5.0	1.2^{d}	

^{a} Data from reference 2. ^{b} $\delta[a(NH_2)]/\delta T = 0.023$ G/K. At 250 K the NH_2 h.f.s. are 0.8 and 1.8 G. ^{c} $\delta[a(NH_2)]/\delta T = 0.021$ G/K. At 270 K the NH_2 h.f.s. are 0.3 and 3.2 G. ^{d} $\delta[a(NH_2)]/\delta T = 0.029$ G/K. At 150 K the NH_2 h.f.s. are 2.2 and 1.9 G.

Table 2. E.s.r. parameters for bis-*N*,*N*-(trimethylsilyl)aminopropynyl radicals $RC{\equiv}C\dot{C}H_{\alpha}N(SiMe_3)_2$ (**8**)

Radical	T/K	H.f.s./G $a(H_{\alpha})$	a(N)	a(other)
(**8a**) R = H	250	15.8	1.6	9.1 (1 H)
(**8b**) R = Me	250	16.5	1.3	11.0 (3 H)
(**8c**) R = Me$_3$Si	250	15.0	1.6	0.3 (9 H)
(**8d**) R = EtO$_2$C	250	13.2	2.4	0.7 (2 H)

primary amines (**1a**—**f**) and di-t-butyl peroxide in t-butylbenzene as solvent for temperatures above *ca.* 210 K and in liquid cyclopropane or dichlorodifluoromethane for lower temperatures. The chloropropynylamine (**1f**) polymerised violently and no spectra could be obtained. The ethoxycarbonyl-substituted amine (**1e**) was unstable and decomposed rapidly even in dilute solution; no interpretable spectra were obtained with this amine either. Amines (**1b**—**d**) gave good spectra which could be unambiguously assigned to the aminopropynyl radicals (**2**); no additional radicals were significant on any of the individual spectra. The e.s.r. hyperfine splittings (h.f.s.) are recorded in Table 1 along with data for (**1a**) which we observed previously.[2]

The *N*,*N*-bis(trimethylsilyl)propynyl amines, (**6**), were examined in a similar way. Good spectra, unambiguously assignable to the corresponding propynyl radicals $RC{\equiv}C\dot{C}HN(SiMe_3)_2$ (**8**), were obtained for R = H, Me, SiMe$_3$, and EtO$_2$C; the e.s.r. h.f.s. are given in Table 2.

For the primary aminopropynyl radicals (**2**) the amino hydrogen h.f.s. were strongly temperature dependent (see below) but the other h.f.s. changed comparatively little. The N h.f.s. were not significantly different from one substituent to another, but the $a(H_{\alpha})$ values increased from R = H to R = Me to R = Bu^{t} (Table 1), indicating higher spin density on the α-carbon as the substituent became a stronger electron repeller. The change is small because the triple bond transmits electronic effects rather poorly. The Me$_3$Si substituent is an attractor[23,24] and the drop in $a(H_{\alpha})$ for (**2d**) is consistent with greater spin delocalisation in this radical. The *N*,*N*-bis(trimethylsilyl)aminopropynyl radicals (**8**) show similar trends (Table 2). The $a(H_{\alpha})$ increases to 16.5 G* for the methyl-substituted radical and decreases below 15.8 G, the h.f.s. of the parent radical (**8a**), for the radicals with electron-withdrawing substituents Me$_3$Si and EtO$_2$C. The h.f.s. for the latter radical (**8d**), which is a true captodative type because of the acceptor substituent, are particularly interesting. The $a(H_{\alpha})$ is very low at 13.2 G and the a(N) value of 2.4 is much higher than for the others in the series. These h.f.s. indicate significantly greater spin delocalisation in this captodative radical.

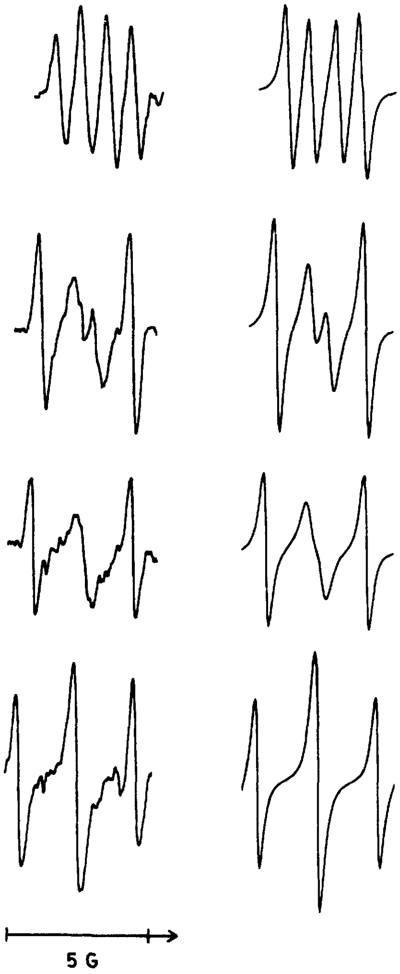


Figure 1. Low-field multiplet from the 9.4 GHz e.s.r. spectrum of 1-amino-3-methylpropynyl radicals (**1b**): (left) experimental spectra, at 250, 284, 295, and 325 K (top to bottom); (right) simulations, with k 2.5 × 10^5, 2.0 × 10^6, 3.0 × 10^6, and 1.3 × 10^7 s^{-1} (top to bottom)

At low temperatures the amino hydrogens of radicals (**2**) are non-equivalent because of restricted rotation about the C–N bond. In the spectra of the methyl-substituted radical (**2b**) the amino hydrogen h.f.s. increased strongly with temperature. As the temperature increases torsional motions about the C–N bond result in more positive spin density reaching the amino hydrogens by a hyperconjugative mechanism. Most probably therefore, both amino hydrogen h.f.s. are positive.[2] Above *ca.* 250 K the spectra from (**2a**) showed exchange broadening due to C–N bond rotation. Figure 1 shows one low-field multiplet from the spectrum of (**2b**) displaying the amino hydrogen splittings. As temperature increases the original double doublet shows broadening of the two central lines which coalesce at *ca.* 290 K and the multiplet finally sharpens up to a triplet when fast rotation makes the two hydrogens equivalent.

The spectral simulations, assuming a two-jump model and using Heinzer's program,[25] are in Figure 1. The best-fit rate constants are given in Arrhenius form in Figure 2 and the Arrhenius parameters are listed in Table 3.

The e.s.r. spectra from the t-butyl-substituted radical (**2c**) exhibited exchange broadening in the temperature range 270—380 K. The spectra were more complex because of the presence of resolved h.f.s. from the nine t-butyl hydrogens. Satisfactory

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* 10G = 1 mT.

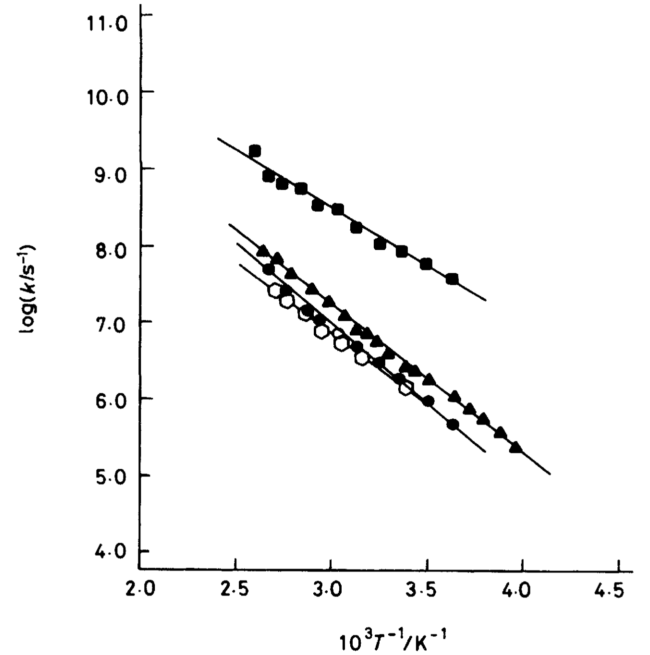

Figure 2. Arrhenius plots of the exchange broadening rate constants from the best-fit simulations of the 1-aminopropynyl radical spectra. Hexagons, (**1a**) (R = H); triangles, (**1b**) (R = Me); squares, (**1c**) (R = Bu^t); circles, (**1d**) (R = Me$_3$Si)

Table 3. Barriers to rotation and stabilisation energies of aminopropynyl radicals $RC{\equiv}C\dot{C}H\alpha NH_2$ (**2**)

Radical	lot (A/s^{-1})	E_2 (kcal mol^{-1})	SE^{MeH} (kcal mol^{-1})
(**2a**) R = H	13.3 ± 1.0	9.7 ± 0.8	24.5
(**2b**) R = Me	12.0 ± 1.0	8.6 ± 0.4	23.4
(**2c**) R = Bu^t	13.0 ± 1.0	6.8 ± 0.6	21.6
(**2d**) R = Me$_3$Si	13.1 ± 1.0	9.3 ± 0.6	24.1

simulations were achieved with a two-jump model; the rate constants are shown in Figure 2 and the Arrhenius parameters are in Table 3. The spectra from the trimethylsilyl substituted radical (**2d**) had a much greater line width which we attribute to unresolved h.f.s. from the nine hydrogens of the Me$_3$Si group. Figure 3 shows one low-field multiplet which displays the amino hydrogen h.f.s. At the low temperature end the two h.f.s. from the non-equivalent amino hydrogens were not fully resolved (partial resolution was achieved at temperatures below those shown in Figure 3) but good correspondence between experimental and simulated spectra was obtained; the rate constants are shown in Figure 2 and the Arrhenius parameters are given in Table 3.

We previously estimated the C–N bond rotation barrier in (**2a**) from line width measurements;[2] more accurate rate constants, obtained by simulation of the spectra, are given in Figure 2 and the corresponding Arrhenius parameters are in Table 3.

The pre-exponential factors (Table 3) are all close to the 'normal' value of 10^{13} s^{-1} for bond rotation and this is good evidence of the reliability of the results. The SE of an aminopropynyl radical is related to the C–N bond rotation barrier E_2 by equation[10] SE(2) = SE(propynyl) + $E_2 - V_2$ where SE(propynyl) is the stabilisation energy of the propynyl unit, and V_2 is the barrier to rotation about the C–N single bond in the absence of delocalisation. Most estimates[10,26] put V_2 at *ca.* 1 kcal mol^{-1}.* The SE of the propynyl radical as calculated from DH°(HC≡CCH$_2$–H)[27,28] is 15.8 kcal mol^{-1} when based on DH°(Me–H), *i.e.* this is the methane-based stabilisation energy,[10,27] Se^{MeH}. Direct thermochemical values of the SEs of substituted propynyl radicals are not available but, by analogy with allyl radicals whose SEs are virtually unchanged by alkyl substitution,[29] we expect the SE(RC≡CCH$_2$•) values for R = H, alkyl, and Me$_3$Si to be essentially equal. We have shown that the SEs of delocalised radicals correlate with the h.f.s. of the terminal hydrogens.[10] In order to observe the effect of our chosen substituents on the h.f.s. of propynyl radicals we generated radicals RC≡CCH$_2$• (**9**) with Bu^t, Me$_3$Si, and EtO$_2$C substituents from the corresponding bromides by bromine abstraction with Me$_3$Sn• radicals. The e.s.r. h.f.s. of these radicals are given in Table 4 together with the known values for other substituents.

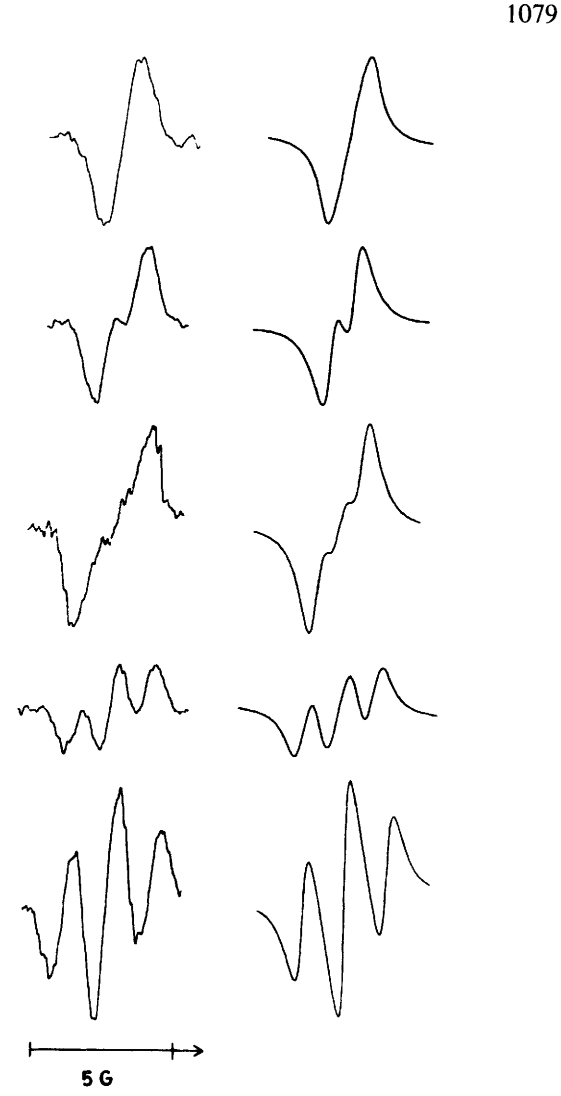

Figure 3. Low-field multiplet from the 9.4 GHz e.s.r. spectrum of 1-amino-3-trimethylsilylpropynyl radicals (**1d**): (left) experimental spectra, at 273, 295, 328, 351, and 384 K (top to bottom); (right) simulations, with k 5.0 × 10^5, 2.0 × 10^6, 8.0 × 10^6, 1.5 × 10^7, and 1.0 × 10^8 s^{-1} (top to bottom)

The small changes in the h.f.s. of the methylene hydrogens in all these radicals support the assumption that the SE of RC≡CCH$_2$• radicals will vary little for alkyl or even Me$_3$Si

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* 1 cal = 4.2 J.

Table 4. E.s.r. Parameters for substituted propynyl radicals $RC{\equiv}CCH_2^{\bullet}$

Radical	T/K	H.f.s./G		Ref.
		$a(H_{\alpha})$	a(other)	
(9a) R = H	150	18.9	12.6 (1 H)	29
(9b) R = Me	205	18.5	12.4 (3 H)	30
(9c) R = Bu^t	160	18.9		*a*
(9d) R = Me_3Si	200	18.4		*a*
(9e) R = EtO_2C	200	18.1	0.7 (2 H)	*a*

[a] This work.

Table 5. E.s.r. parameters for substituted hydroxypropynyl radicals $RC{\equiv}\dot{C}HOH$ (**4**)

Radical	T/K	H.f.s./G		
		$a(H_{\alpha})$	a(OH)	a(other)
(4a) R = H^b	298	17.8	0.9	9.7 (1 H)
(4b) R = Me	300	18.0	0.8	11.3 (3 H)
(4c) R = Bu^t	300	18.0	1.0	0.34 (9 H)
(4d) R = Me_3Si	300	17.1	1.1	0.26 (9 H)
(4e) R = CF_3	300	17.1	1.7	16.3 (3 F)
(4f) R = EtO_2C	300	15.8	1.9^a	0.66 (2 H)^a

[a] Measurement at 300 K. [b] Ref. 31.

Table 6. Substituent parameters for propynyl radicals $R^1C{\equiv}\dot{C}HR^2$

Radical	R^1	R^2	Z	Z^{calc}
	H	H	0.000	
(2a)	H	NH_2	0.222	
(8a)	H	$N(SiMe_3)_2$	0.164	
(4a)	H	OH	0.058	
(9b)	Me	H	0.021	
(9c)	Bu^t	H	0.000	
(9d)	Me_3Si	H	0.026	
(9e)	EtO_2C	H	0.042	
(2b)	Me	NH_2	0.180	0.238
(2c)	Bu^t	NH_2	0.164	0.222
(2d)	Me_3Si	NH_2	0.243	0.242
(8b)	Me	$N(SiMe_3)_2$	0.127	0.182
(8c)	Me_3Si	$N(SiMe_3)_2$	0.206	0.186
(8d)	EtO_2C	$N(SiMe_3)_2$	0.302	0.199
(4b)	Me	OH	0.048	0.078
(4c)	Bu^t	OH	0.048	0.058
(4d)	Me_3Si	OH	0.095	0.082
(4e)	CF_3	OH	0.095	
(4f)	EtO_2C	OH	0.164	0.098

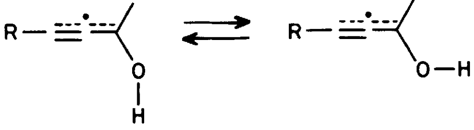
substituents. The SEs given in Table 3 were calculated using the same value *i.e.* 15.8 kcal mol^{-1} for all the propynyl units.

The SE^{MeH} of the aminomethyl radical is[1] 10 kcal mol^{-1} and hence SE^{MeH}(propynyl) + SE^{MeH}(aminomethyl) = 25.8 kcal mol^{-1} *i.e.* this represents the sum of the stabilising effects of the two substituents at the radical centre in (**2a**). The experimental SEs of disubstituted radicals with π-delocalisation but without captodative substitution are normally significantly less (by 4—10 kcal mol^{-1}) than the sum of the SEs due to the separate substituents.[10] The ethynyl group is a weak acceptor and therefore (**2a**) is itself weakly captodative in character. The measured SE^{MeH} (Table 3) of (**2a**) is only marginally less than the sum of the SEs of the two substituents and hence this result supports the proposal that captodative substitution leads to extra stabilisation. The Me and Bu^t substituents in (**2b** and **c**) are elctron repellers and would be expected to weaken the captodative stabilisation. Table 3 shows that the measured SE^{MeH} values are lower for these two radicals. In fact the reduction is surprisingly large, particularly for (**2c**). The Me_3Si group is weakly electron attracting and therefore a slight increase in the SE^{MeH} would be expected for (**2d**). Table 3 shows that SE^{MeH} (**2d**) is greater than those of (**2b** and **c**) but equal to that of (**2a**) to within the experimental error. A more rigorous test of the captodative stabilisation proposal requires the observation of aminopropynyl radicals with strong acceptor stubstituents R *e.g.* (**2e**). Unfortunately we were unable to observe spectra from the precursor of this radical (see above) and therefore our conclusions cannot be more positive than those stated above.

E.s.r. Spectra of Substituted Hydroxypropynyl Radicals.—Good spectra of the corresponding hydroxypropynyl radicals were obtained on hydrogen abstraction from the alcohols (**3**) by t-butoxyl radicals. No additional radicals were detectable. The e.s.r. parameters for (**4a**—**f**) are recorded in Table 5. The $a(H_{\alpha})$ values show a slight increase when the substituent is an electron repeller (*e.g.* Me and Bu^t), and a small decrease when the substituent is an electron attractor (Me_3Si, CF_3).

The captodative substituted radical (**4f**), *i.e.* R = CO_2Et, shows a large decrease in $a(H_{\alpha})$ together with the highest a(OH) value. The pattern of spin distribution revealed by Table 5 is certainly consistent with the idea that captodative substitution leads to extra delocalisation and stabilisation.

The radicals (**4**) are capable of existing in two conformations (**10a** and **b**) which would interconvert by rotation about the bond. Exchange broadening might be expected as a result of this process. The e.s.r. spectra were examined over a wide temperature range but no line broadening was observed except for (**4b** and **f**) at *ca.* 120 K. At this temperature the hydroxyacetylenes are very insoluble in CF_2Cl_2 and in hydrocarbons, and we attribute the observed broadening to anisotropic tumbling. Exchange broadening was observed by Krusic and his co-workers[32] in the spectra of the $^{\bullet}CH_2OH$ radical with coalescence at *ca.* 165 K. The barrier to rotation about the C–O bond was found to be 4.6 kcal mol^{-1}. In the hydroxypropynyl radicals (**4**) delocalisation of the unpaired electron on to the propynyl unit will remove electron density from the C–O bond so that lower rotation barriers are expected. It is probable, therefore, that exchange broadening in the spectra of radicals (**4**) occurs at temperatures too low for detection.



(**10a**) (**10b**)

The hydroxyl hydrogen h.f.s. of radicals (**4**) showed a steady decrease in magnitude with increasing temperature. Hence, a(OH) is probably negative and this is in agreement with the sign of a(OH) found for the hydroxymethyl radical.[32,33] In fact for (**4b**) a(OH) was monitored up to 440 K and was found to decrease from 1.3 G at 240 K to zero at 400 K, subsequently increasing again to 0.5 G at 440 K.

Recently, Arnold and his co-workers[34] made a comprehensive study of the e.s.r. spectra of substituted benzyl radicals and quantified the delocalising effect of the substituents in terms of substituent parameters σ. A similar treatment can be given for our substituted propynyl radicals $R^1C{\equiv}\dot{C}HR_2$, defining $Z(R^1,R^2)$ as follows: $Z(R^1,R^2) = 1 - [a(R^1,R^2)/a(H,H)]$. Z(H,H) is zero by definition. For a disubstituted radical the

$Z(\mathrm{R}^1,\mathrm{R}^2)$ value can be calculated from the substituent constants of the mono-substituted radicals: $Z(\mathrm{R}^1,\mathrm{R}^2)^{\mathrm{calc}} = 1 - [1 - Z(\mathrm{R}^1,\mathrm{H})][1 - Z(\mathrm{H},\mathrm{R}^2)]$. The experimental and calculated substituent parameters for the series of propynyl radicals are collected in Table 6.

Examination of Table 6 shows that for R^1 = Me or Bu^t the experimental Z value is always less than the calculated value *i.e.* the resultant effect is less than additive. This is in agreement with the SE results.[10] For the attractor substituent R^1 = $\mathrm{Me_3Si}$, the experimental Z value slightly exceeds the calculated value, but for the two radicals with R^1 = $\mathrm{EtO_2C}$, **(8d)** and **(4f)**, *i.e.* those with full captodative character, the experimental Z value greatly exceeds Z^{calc}. This combination of substituents leads to a 'greater than additive' effect which is fully in accord with the view that captodative substitution leads to an 'extra' stabilisation.

Experimental

E.s.r. spectra were recorded with a Bruker ER 200D spectrometer on degassed samples, sealed in Spectrosil tubes, irradiated with light from a 500 W super-pressure Hg arc. Routine n.m.r. spectra were obtained with a Bruker WP 80 instrument for $\mathrm{CDCl_3}$ solutions at room temperature with $\mathrm{Me_4Si}$ as internal standard.

But-2-ynylamine[35] **(1b)**.—To a suspension of potassium phthalimide (14.4 g) in dimethylformamide (DMF) (150 ml) was added 1-bromobut-2-yne (8.0 g). The solution was stirred overnight, diluted with water (750 ml), and extracted with $\mathrm{CHCl_3}$ (2 × 150 ml). The $\mathrm{CHCl_3}$ solution was washed with NaOH (200 ml; 0.5%) and water (200 ml), dried ($\mathrm{Na_2SO_4}$), and the solvent was removed on a rotary evaporator. The phthalyl derivative (57%) was recrystallised from acetone–light petroleum (b.p. 40—60 °C); δ_H 1.8 (3 H, t), 4.4 (2 H, q), and 7.6—7.8 (4 H, m). To the phthalyl derivative (6.3 g) in EtOH (250 ml) was added hydrazine hydrate (3.5 g) and the solution was stirred overnight. After dilution with water (75 ml) and adjustment of the pH to 3.5 with concentrated HCl the phthalyl hydrazide was filtered off and the solvent evaporated under reduced pressure. The residual solution was diluted with water (100 ml), basified with NaOH (30 ml; 10M) and extracted with $\mathrm{CHCl_3}$. After drying ($\mathrm{Na_2SO_4}$) the $\mathrm{CHCl_3}$ was distilled off at atmospheric pressure and the residue was distilled, b.p. 112 °C; yield 53%; δ_H 1.3 (2 H, s), 1.6 (3 H, t), and 3.1 (2 H, q); δ_C 3.8 (q), 36.3 (t), 74.6 (s), and 83.7 p.p.m. (s).

1,1,3-Tris(trimethylsilyl)prop-2-ynylamine **(6d)**.—To *N,N*-bis(trimethylsilyl)propynylamine[36,37] under $\mathrm{N_2}$ cooled to −78 °C in dry ether (200 ml) was added Bu^{n}Li (7.8 ml; 1.6M hexane solution) followed by $\mathrm{Me_3SiCl}$ (1.9 g). The solution was stirred and allowed to warm to room temperature over 5 h. Ethyl acetate (1 ml) was added and the mixture was filtered through Hyflo Supercel. The solvent was removed on a rotary evaporator and the residue distilled, b.p. 160 °C at 20 Torr; yield 76%; δ_H 0.12 (27 H, s) and 3.5 (2 H, s); δ_C 1.6 (q), 34.8 (t), 86.1 (s), and 108.8 p.p.m. (s).

3-Trimethylsilylprop-2-ynylamine **(1d)**.—HCl Gas was bubbled through a solution of **(6d)** (4.0 g) in wet ether (150 ml). The precipitated hydrochloride was filtered off, washed (ether), and dried; yield 2.5 g; $\delta_H(\mathrm{D_2O})$ 0.19 (9 H, s) and 3.83 (2 H, s). The hydrochloride (1.5 g) was suspended in $\mathrm{CHCl_3}$ and cooled in ice while $\mathrm{NH_3}$ gas was bubbled through. The $\mathrm{NH_4Cl}$ was filtered off and the solution dried ($\mathrm{Na_2SO_4}$). Evaporation of the solvent gave pure amine in 95% yield; δ_H 0.15 (9 H, s), 1.4 (2 H, s), and 3.41 (2 H, s); δ_C 0.0 (q), 32.4 (t) 86.2 (s), and 107.7 p.p.m. (s).

N,N-Bis(trimethylsilyl)but-2-ynylamine **(6b)**.—To *N,N*-bis(trimethylsilyl)propynylamine (1.5 g) in dry THF (50 ml) was added Bu^{n}Li (4.9 ml; 1.6M hexane solution) followed by $\mathrm{CH_3I}$ (1.6 g). The solution was refluxed overnight, cooled, poured onto ice (100 g), and extracted with ether (3 × 100 ml). The combined ether extracts were dried ($\mathrm{Na_2SO_4}$), decolourised with charcoal, and the ether was removed on a rotary evaporator. The product was distilled, b.p. 150 °C at 20 Torr; yield 31%; δ_H 0.15 (18 H, s), 1.8 (3 H, t), and 3.5 (2 H, q).

Ethyl 3-[N,N-Bis(trimethylsilyl)amino]prop-1-yne-1-carboxylate **(6e)**.—To *N,N*-bis(trimethylsilyl)aminopropyne (2.0 g) in dry ether (100 ml) cooled to −78 °C under $\mathrm{N_2}$ was added Bu^{n}Li (6.2 ml; 1.6M hexane solution) followed by ethyl chloroformate (1.0 ml). The solution was stirred and allowed to warm to room temperature over 3 h. Ethyl acetate (1.0 ml) was added and the solution was filtered through Hyflo Supercel. The solvent was removed on a rotary evaporator and the residue filtered (Hyflo Supercel) and distilled; b.p. 135 °C at 2.5 Torr; yield 41%; δ_H 0.15 (18 H, s), 1.28 (3 H, t), 3.4 (2 H, s), and 3.93 (2 H, q); δ_C 1.6 (q), 14.1 (q), 34.3 (t), 61.6 (t), 74.5 (s) 89.4 (s), and 153.7 p.p.m. (s).

Ethyl 3-Aminoprop-1-yne-1-carboxylate **(1e)**.—Dry HCl gas was bubbled through **(6e)** (2.0 g) in isopropyl alcohol–dry ether (1:1; 20 ml) cooled in ice. Additional ether (40 ml) was added to fully precipitate the hydrochloride. The product was filtered off and pumped dry; yield 92%. The hydrochloride was dissolved in $\mathrm{CH_2Cl_2}$ (40 ml), $\mathrm{Na_2SO_4}$ was added, and dried $\mathrm{NH_3}$ gas was bubbled through the mixture for 10 min at 0 °C. The solution was filtered and the solvent removed at 0 °C on an oil-pump; δ_H 1.3 (3 H, t), 1.43 (2 H, s), 3.55 (2 H, s), and 4.25 (2 H, q). The lifetime of the amine was < 1 h in the open laboratory.

3-Chloro-N,N-bis(trimethylsilyl)prop-2-ynylamine **(6f)**.—To *N,N*-bis(trimethylsilyl)propynylamine (5.0 g) in dry ether (200 ml) under $\mathrm{N_2}$ at −78 °C was added Bu^{n}Li (15.5 ml; 1.6M hexane solution) followed by *N*-chlorosuccinimide (3.4 g). The temperature was allowed to rise overnight and ethyl acetate (1 ml) was added and the solution was filtered through Hyflo Supercel. The solvent was removed on a rotary evaporator and the residue was distilled, b.p. 160 °C at 20 Torr; yield 77%; δ_H 0.13 (18 H, s) and 3.53 (2 H, s); δ_C 1.6 (q), 34.4 (t), 59.4 (s), and 71.0 p.p.m. (s).

3-Chloroprop-2-ynylamine **(1f)**.—HCl Gas was bubbled through a solution of **(6f)** (2.1 g) in isopropyl alcohol–dry ether (1:1; 25 ml) cooled in ice. The resulting hydrochloride precipitate was filtered off and dried in a vacuum desiccator; yield 97%. Ammonia gas was bubbled through an ice-cold suspension of the hydrochloride (1.1 g) in $\mathrm{CH_2Cl_2}$ (50 ml). The solution was dried ($\mathrm{Na_2SO_4}$), decolourised with charcoal, and the solvent removed on a rotary evaporator; yield 90%; δ_H 1.38 (2 H, s) and 3.43 (2 H, s). The neat liquid polymerised explosively on standing.

4,4-Dimethylpent-2-yn-1-ol **(3c)**.—To an ice-cold solution of 3,3-dimethylbut-1-yne (10.0 g) in dry ether (50 ml) was added Bu^{n}Li (75 ml; 1.6M hexane solution) and dry THF (40 ml). The solution was warmed to room temperature and paraformaldehyde (4.6 g) was added in portions over 45 min. The mixture was refluxed for 4 h, cooled, poured into water, and shaken vigorously. The aqueous layer was extracted with ether (4 × 30 ml), the combined organic layers were washed with saturated $\mathrm{NH_4Cl}$ solution, dried ($\mathrm{Na_2SO_4}$), and the solvent was removed and the residue distilled, b.p. 80 °C; yield 69%; δ_H 1.25 (9 H, s), 3.7 (1 H, s), and 4.3 (2 H, s); δ_C 27.5 (s), 31.1 (q), 50.5 (t), 77.4 (s), and 93.9 p.p.m. (s).

1-Bromo-4,4-dimethylpent-2-yne was made from **(3c)** as described in the literature,[38] b.p. 60—64 °C at 20 Torr.

4,4-Dimethylpent-2-ynylamine[35] **(1c)** was prepared from the above bromide by the same method as for (**1b**); yield 62%; δ_H 1.25 (9 H, s), 3.5 (2 H, s), and 3.7 (2 H, s); δ_C 27.4 (s), 31.2 (q), 31.7 (t), 79.1 (s), and 90.8 p.p.m. (s).

3-*Trimethylsilylprop*-2-*yn*-1-*ol* (**3d**).—To the THP ether of prop-2-ynyl alcohol[22] (3.5 g) in dry ether (100 ml) at −78 °C under N_2 was added Bu^{n}Li (16 ml; 1.6M hexane solution) followed by trimethylsilyl chloride (3.9 g). The solution was allowed to warm to room temperature overnight then poured into ice–water (100 ml) and extracted with ether (3 × 100 ml). The combined ethereal layers were dried (Na_2SO_4), filtered, and the solvent was removed on a rotary evaporator. The residue was distilled (b.p. 200 °C at 20 Torr) to give 80% of the THP ether of trimethylsilylprop-2-ynyl alcohol; δ_H 0.2 (9 H, s), 1.7 (6 H, m), 3.3—4.0 (2 H, m), 4.3 (2 H, s), and 4.85, (1 H, s). The THP ether (4.0 g) and pyridinium toluene-*p*-sulphonate[22] (0.4 g) in ethanol (100 ml) were stirred at 55 °C for 5 h. The ethanol was removed on a rotary evaporator, water (100 ml) was added, and the mixture was extracted with ether (5 × 100 ml). The combined ether extracts were dried (Na_2SO_4), the ether was removed, and the residue distilled, b.p. 120 °C at 20 Torr; yield 54%; δ_H 0.2 (9 H, s), 2.12 (1 H, br s), and 4.3 (2 H, s).

1-*Bromo*-3-*trimethylsilylprop*-2-*yne*.—To alcohol (**3d**) (0.7 g) and Et_3N (0.56 g) in dry CH_2Cl_2 (30 ml) under N_2 and cooled in ice, was added CH_3SO_2Cl (0.7 g) dropwise. The solution was stirred for 15 min, water was added, and the CH_2Cl_2 layer was washed with 2M-HCl, brine, and $NaHCO_3$ and dried (Na_2SO_4). The solvent was removed at room temperature on a rotary evaporator. An i.r. spectrum showed the acetylenic band at 2 190 and the SO_2 bands at 1 360 and 1 175 cm^{-1}. The methanesulphonate was added to LiBr (1.5 g) in dry acetone (35 ml) and the solution was refluxed for 1 h. The precipitate was filtered off, the acetone was removed on a rotary evaporator, and water was added to dissolve unchanged LiBr. The mixture was extracted with light petroleum (b.p. 40—60 °C) (5 ml), dried (Na_2SO_4), and chromatographed on silica gel. The bromide was eluted with light petroleum (400 ml). The solvent was removed and the residue distilled, b.p. 90 °C; yield 77%; δ_H 0.17 (9 H, s) and 3.93 (2 H, s); M^+ (obs) 189.9807. Calc. for $C_6H_{11}Si^{79}Br$: M 189.9814.

Ethyl 3-*Hydroxyprop*-1-*yne*-1-*carboxylate* (**3f**).—This was prepared from the THP ether of prop-2-ynyl alcohol and ethyl chloroformate by the method described above for (**3d**); yield 55%; b.p. 103—104 °C at 2 Torr; δ_H 1.33 (3 H, t), 4.2 (1 H, br s), 4.37 (2 H, q), and 4.51 (2 H, br s).

Ethyl 3-*Bromoprop*-1-*yne*-1-*carboxylate*.—This was prepared from (**3f**) by treatment of the methanesulphonate with LiBr using the procedure described above; b.p. 105 °C at 0.5 Torr; yield 93%; δ_H 1.33 (3 H, t), 4.08 (2 H, s), and 4.33 (2 H, q); δ_C 12.1 (t), 14.0 (q), 62.4 (t), 77.4 (s), 81.6 (s), and 152.8 (s).

4,4,4-*Trifluorobut*-2-*yn*-1-*ol* (**3e**).—3,3,3-Trifluoropropyne (5 g) was bubbled through a solution of Bu^{n}Li (35 ml; 1.6M hexane solution) in dry ether (65 ml) under N_2 at −78 °C with a 'dry ice' condenser attached. Paraformaldehyde (2.3 g) was added and the mixture was allowed to warm to room temperature overnight. The solution was poured into ice–water (200 g), shaken, and extracted with ether (5 × 150 ml). The combined ether layers were washed with saturated NH_4Cl solution, dried (Na_2SO_4), decolourised with charcoal, and the ether was removed. The residue was distilled; b.p. 80 °C at 100 Torr; yield 32%; δ_H 2.2 (1 H, br s) and 4.4 (2 H, q). Attempts to convert this alcohol into the corresponding bromide were unsuccessful.

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References

1 D. Griller and F. P. Lossing, *J. Am. Chem. Soc.*, 1981, **103**, 1586.
2 D. Griller, D. C. Nonhebel, and J. C. Walton, *J. Chem. Soc., Perkin Trans. 2*, 1983, 1373.
3 D. Griller, J. A. Howard, P. R. Marriot, and J. C. Scaiano, *J. Am. Chem. Soc.*, 1981, **103**, 619.
4 K. A. McLauchlan and A. J. D. Ritchie, *J. Chem. Soc., Perkin Trans. 2*, 1984, 275.
5 J. C. Scaiano, *J. Phys. Chem.*, 1981, **85**, 2851.
6 P. J. Wagner, *Top. Curr. Chem.*, 1976, **66**, 1.
7 P. Neta and R. Fessenden, *J. Phys. Chem.*, 1971, **75**, 738.
8 L. R. Easton and M. P. Hay, *J. Chem. Soc., Chem. Commun.*, 1986, 55.
9 H. Paul and H. Fischer, *Helv. Chim. Acta*, 1971, **54**, 485.
10 J. C. Walton, *Rev. Chem. Intermed.*, 1984, **5**, 249.
11 M. J. S. Dewar, *J. Am. Chem. Soc.*, 1952, **74**, 3353.
12 R. W. Baldock, P. Hudson, A. R. Katritzky, and F. Sati, *J. Chem. Soc., Perkin Trans. 1*, 1974, 1422, 1427.
13 A. T. Balaban, M. T. Capriou, N. Negoita, and R. Bairou, *Tetrahedron*, 1977, **33**, 2249.
14 H. G. Aurich and E. Deuschle, *Liebigs Ann. Chem.*, 1981, 719.
15 H. G. Viehe, R. Merenyi, L. Stella, and Z. Janousek, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 917.
16 A. de Mesmaeker, L. Vertommen, R. Merenyi, and H. G. Viehe, *Tetrahedron Lett.*, 1982, **23**, 69.
17 R. Merenyi, A. de Mesmaeker, and H. G. Viehe, *Tetrahedron Lett.*, 1983, **24**, 2765.
18 H. G. Viehe, Z. Janousek, R. Merenyi, and L. Stella, *Acc. Chem. Res.*, 1979, **18**, 148.
19 B. Giese and J. Meixner, results quoted in ref. 11.
20 M. Zamkanei, J. H. Kaiser, R. Birkhofer, H. D. Beckhaus, and Ch. Ruchardt, *Chem. Ber.*, 1983, **116**, 3216.
21 R. J. P. Corriu, V. Nuynh, J. Iqbal, and J. E. J. Moreau, *J. Organomet. Chem.*, 1984, **276**, C61.
22 N. Myashita, A. Yoshikoshi, and P. A. Grieco, *J. Org. Chem.*, 1977, **42**, 3772.
23 M. Kira, M. Watanabe, and H. Sakurai, *J. Am. Chem. Soc.*, 1977, **99**, 7780; 1980, **102**, 5202.
24 P. J. Barker, A. G. Davies, R. Henriques, and J.-Y. Nedelec, *J. Chem. Soc., Perkin Trans. 2*, 1982, 745.
25 J. Heinzer, Quantum Chemistry Program Exchange, No. 209, University of Indiana, Indiana, 1972.
26 H.-G. Korth, H. Trill, and R. Sustmann, *J. Am. Chem. Soc.*, 1981, **103**, 4483.
27 K. D. King, *Int. J. Chem. Kinet.*, 1978, **10**, 545; K. D. King and T. T. Nguyen, *J. Phys. Chem.*, 1979, **83**, 1940; T. T. Nguyen and K. D. King, *ibid.*, 1981, **85**, 3130.
28 W. Tsang, *Int. J. Chem. Kinet.*, 1978, **10**, 687.
29 A. B. Trenwith, *J. Chem. Soc., Faraday Trans. 1*, 1973, **69**, 1737.
30 R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 1963, **39**, 2147.
31 J. K. Kochi and P. J. Krusic, *J. Am. Chem. Soc.*, 1970, **92**, 4110.
32 P. J. Krusic, P. Meakin, and J. P. Jesson, *J. Phys. Chem.*, 1971, **75**, 3438.
33 J. K. Kochi, *Adv. Free Radical Chem.*, 1975, **5**, 189.
34 J. H. Dust and D. R. Arnold, *J. Am. Chem. Soc.*, 1983, **105**, 1221, 6531; D. R. Arnold, A. M. de P. Nicholas, and M. S. Snow, *Can. J. Chem.*, 1985, **63**, 1150; D. D. M. Wayner and D. R. Arnold, *ibid.*, p. 2378.
35 A. F. M. McKay, D. L. Garmaise, R. Gaudry, H. A. Baker, G. Y. Paris, R. W. Kay, G. E. Just, and R. Schwartz, *J. Am. Chem. Soc.*, 1959, **81**, 4328.
36 R. J. P. Corriu, V. Huynh, and J. J. E. Moreau, *Tetrahedron Lett.*, 1984, **25**, 1887.
37 H. J. Bestman and G. Wolfel, *Chem. Ber.*, 1984, **117**, 1250.
38 L. Brandsma, 'Preparative Acetylenic Chemistry,' Elsevier, Amsterdam, 1971, Ch. 8, p. 158.

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