Hydrogen Abstraction from Primary Amines. Substituent Effects on the Carbon–Nitrogen Bond Rotation Barriers in Aminoalkyl Radicals

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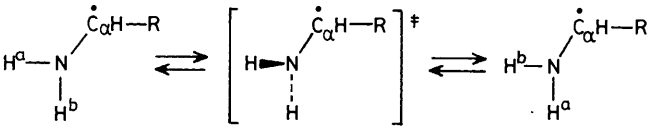
Hydrogen abstraction by t-butoxyl radicals from primary amines RCH_2NH_2 (R = H, Me, Et, Pr^i, or Bu^t) gave mainly α-aminoalkyl radicals which were observed by e.s.r. spectroscopy. The barriers to rotation about the C–N bonds were determined from exchange broadening. For 2-fluoro- and 2-chloro-ethylamine the initial α-aminoalkyl radical lost hydrogen halide to give a mixture of *syn*- and *anti*-1-aza-allyl radicals. In contrast, the 1-amino-2,2,2-trifluoroethyl radical was stable under the same experimental conditions. The α-amino radicals formed on hydrogen abstraction from the methyl and t-butyl esters of glycine and the t-butyl ester of alanine were also examined. The stabilisation energy of the α-aminomethyl radical was estimated from the C–N bond rotation barriers of the aminoalkyl radicals. The pattern of stabilisation was found to be consistent with an extra stabilisation in radicals with captodative substitution.

Free-radical reactions of amines have aroused considerable interest because of their importance in radiation chemistry and because of the significance of amino acid-derived radicals in biochemistry. The reactions of aliphatic amines with hydroxyl radicals generated by the Ti^{III}–H_2O_2 system in aqueous solution have been studied by several groups.[1–5] In alkaline solution the main radicals detected from primary amines were aminoalkyls, $R^1R^2\dot{C}NH_2$, derived by hydrogen abstraction at the carbon atom adjacent to the amino group (C_α). Product studies also showed that the main attack occurred at C_α.[5–8] t-Butoxyl radicals abstract hydrogen at C_α in primary and tertiary amines to give aminoalkyl radicals[9] but, under certain conditions, aminyl radicals can also be detected with secondary amines.[8] Free-radical attack on glycine and other amino acids occurs at C_α[4,10] and the corresponding radicals have been observed in single crystals[11,12] and in aqueous solution.[4,13] Aminoalkyl radicals also react with ketones to give ketyls in one of the fastest known radical reactions.[14] The preferential H-abstraction at C_α in amines by HO$^\bullet$, RO$^\bullet$, and ketone triplets has been attributed to a favourable polar effect from the NH_2 group and to thermodynamic stabilisation (but not kinetic stabilisation) of the aminoalkyl radicals by conjugation of the unpaired electron with the nitrogen lone pair.[9] Mass spectrometric studies showed that the methane-based stabilisation energies[15,16] of $H_2NCH_2^\bullet$ and $Me_2NCH_2^\bullet$ were large (10 and 20 kcal mol^{-1}* respectively).[17]

Although the course of H-abstraction from amines by t-butoxyl and other radicals is well understood and the kinetics have been investigated,[9,18] difficulty has been experienced in directly observing aminoalkyl radicals by e.s.r. spectroscopy.[5,9] For this reason McLauchlan and his co-workers used laser flash photolysis of a benzene solution of benzene-1,2:4,5-tetracarboxylic dianhydride and a tertiary amine to produce spin-polarised radicals of the type $^\bullet CH_2NR_2$ which could be directly observed because of the increased intensity.[19] We showed that 1-aminoallyl and 1-aminopropynyl radicals could be observed by conventional e.s.r. when generated photochemically from amines by t-butoxyl radicals.[20] In the transition state (**2**) for rotation about the C–N bond in the aminoalkyl radical (**1**) the unpaired electron is confined to the alkyl unit and any stabilisation due to conjugation with the nitrogen lone pair is



(**1**) (**2**)

lost. The stabilisation energies (SEs) of aminoalkyl radicals are therefore related to the C–N bond rotation barriers. We showed that in one case, that of the aminopropynyl radical, $H_2N\dot{C}HC{\equiv}CH$, the rotation barrier could be determined from the exchange broadening in the e.s.r. spectra.[20] We have subsequently undertaken a study of a range of aminoalkyl radicals in order to observe the influence of various substituents in the alkyl unit on the distribution of unpaired spin and on the C–N rotation barriers and to assess the extent of their stabilisation. We reported the results for the radicals $R_3C\dot{C}HNH_2$ (R = H or Me) and for Bu^{t}OC(O)$\dot{C}$HNH$_2$ in preliminary form.[21] This paper gives a full account of the e.s.r. observations on the preceding radicals together with additional results for a wider range of substituents.

Results and Discussion

Hydrogen Abstraction from Alkylamines: Aminoalkyl Radicals.—The radicals were generated by photolysis of a solution of the primary amine RCH_2NH_2 (R = H, Me, Et, Pr^i, or Bu^t) and di-t-butyl peroxide in t-butylbenzene, or in neat di-t-butyl peroxide, in the cavity of the e.s.r. spectrometer. In each case the only species with significant spectral intensity was the aminoalkyl radical, $R\dot{C}HNH_2$, and no other radicals could be identified. Abstraction from methylamine gave aminomethyl radicals. The hyperfine splittings (h.f.s.) (see Table 1) from the nitrogen and the α-hydrogens showed small increases with increasing temperature but the amino group hydrogen h.f.s., $a(NH_2)$, showed a very large increase from 0.63 G† at 128 K to 2.57 G at 250 K. The h.f.s. were in agreement with the literature[4] at ambient temperature. The fact that $a(NH_2)$ *increases* with increasing temperature is good evidence that this h.f.s. is positive.[20]

The α-aminoethyl radical, generated from ethylamine,

* 1 cal ≡ 4.2 J.

† 1 G ≡ 0.1 mT.

Table 1. E.s.r. hyperfine splittings (G) of aminoalkyl $R\dot{C}_{\alpha}HNH_2$ and related radicals

Radical	Temp. (K)	$a(H_\alpha)$	$a(NH^1)$	$a(NH^2)$	$a(N)$	$a(H_\beta)$	$a(H_\gamma)$	a(other)
$H\dot{C}HNH_2$	228	14.76 (2 H)	2.29	2.29	5.41			
$CH_3\dot{C}HNH_2$	228	14.7	2.5	5.45	4.4	20.7 (3 H)		
$CH_3CH_2\dot{C}HNH_2$	240	14.8	2.3	5.5	4.5	20.0 (2 H)	0.6 (3 H)	
$(CH_3)_2CH\dot{C}HNH_2$	228	14.7	2.2	5.5	4.5	20.2 (1 H)		
$(CH_3)_3C\dot{C}HNH_2$	228	14.6	1.7	6.2	4.3			
$CF_3\dot{C}HNH_2$	228	15.5	(−) 2.5	(−) 0.7	6.2			36.1 (3 F)
$Bu^tO_2C\dot{C}HNH_2$	228	13.2	(−) 5.2	(−) 4.7	6.0			
$CH_3O_2C\dot{C}HNH_2$	306	13.0	5.4	3.8	6.3			1.6 (3 H)
$Bu^tO_2C\dot{C}(CH_3)NH_2$	262		4.0	2.6	5.2	13.2 (3 H)		

Table 2. C–N Bond rotation barriers of substituted aminoalkyl radicals

	$H_2N\dot{C}_{\alpha}HR$	
R	log A/s^{-1}	E/kcal mol^{-1}
H		
CH_3	13.2 ± 0.4	7.6 ± 0.4
CH_3CH_2[a]	~13	~7.5
$(CH_3)_2CH$	13.1 ± 0.4	7.3 ± 0.4
$(CH_3)_3C$	13.4 ± 0.4	7.5 ± 0.2
CF_3	13.4 ± 0.2	10.9 ± 0.6
Bu^tOCO	13.2 ± 0.5	14.9 ± 1.2
$HC{\equiv}C$[b]	13.8 ± 0.7	10.5 ± 1.2
$N{\equiv}C$[b]		11 ± 2

[a] Estimated from the coalescence temperature. [b] From ref. 20.

showed non-equivalent h.f.s. from the two amino hydrogens (Table 1) both of which increased with temperature. The spectra exhibited exchange broadening due to rotation about the C–N bond in the temperature range 230—310 K with coalescence at *ca.* 260 K. Spectra were simulated assuming a two-jump model and using a modified version of Heinzer's program.[22] The rotation barrier was found by comparison of the simulated and experimental spectra and is given in Table 2. The 1-aminopropyl radical, $CH_3CH_2CHNH_2$, was observed on H-abstraction from 1-aminopropane and the h.f.s. are in Table 1. Exchange broadening was observed in the same temperature range as for the 1-aminoethyl radical but a small splitting from the δ-CH_3 hydrogens was partly resolved and this made the spectra too weak and complex to analyse in the region of the line broadening. Good spectra were obtained for 1-aminoisobutyl, $Me_2CH\dot{C}HNH_2$ and 1-aminoneopentyl radicals, $Bu^t\dot{C}HNH_2$, and the h.f.s. are in Table 1. The NH_2 hydrogens were non-equivalent at low temperatures but became equivalent at high temperatures because rotation about the C–N bond became fast on the e.s.r. timescale. The resultant exchange broadening was simulated, as above, and the rotation barriers are in Table 2.

Hydrogen Abstraction from 2-Halogenoalkylamines.—The e.s.r. spectra obtained on H-abstraction by t-butoxyl radicals from 2,2,2-trifluoroethylamine showed h.f.s. from three fluorines, a nitrogen atom, and three non-equivalent hydrogen atoms. This radical, which can readily be identified as $CF_3\dot{C}HNH_2$ (Table 1), showed unique changes in the spectrum with increasing temperature. Some of the variations are shown in the Figure. At 240 K the two non-equivalent amino hydrogens gave the expected double doublet, but at 290 K this became a simple doublet which evolved into a broadened double doublet at 320 K, a broadened triplet at 330 K, a broadened doublet at 359 K, and finally a broadened triplet at 369 K.

These changes can be explained in the following manner. At 240 K and below the two amino hydrogens are non-equivalent

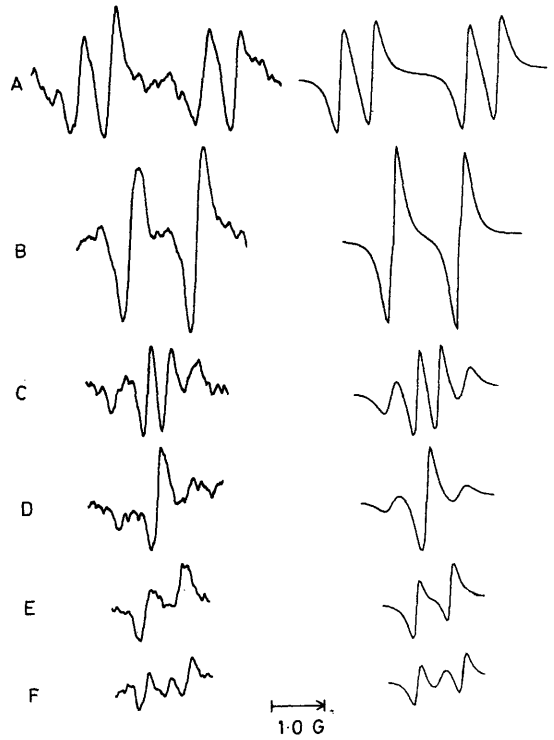
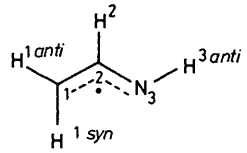
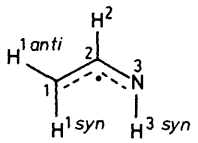
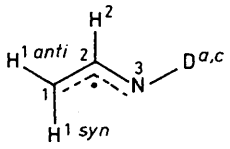
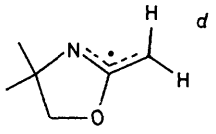


Figure. Low-field multiplet from the 9.4 GHz e.s.r. spectrum of 1-amino-2,2,2-trifluoroethyl radicals. Left-hand side, experimental spectra: A, 240; B, 290; C, 320; D, 330; E, 359; F, 369 K. Right-hand side, simulations with, from the top 10^{-6} k 0.0, 0.2, 1.5, 2.2, 10.0, and 20.0 s^{-1}

with *negative* h.f.s. thus giving a double doublet splitting. The two hydrogens experience different average environments and, as the temperature increases, torsional motions about the C–N bond will result in more positive spin density reaching them by a hyperconjugative mechanism. Both h.f.s. increase in absolute magnitude so that at 290 K one becomes zero while the other is still negative and a doublet results. At 320 K the double doublet is due to two unequal h.f.s. of opposite sign. The positive h.f.s. continues to increase and the other also becomes less negative (*i.e.* decreases in magnitude) but at the same time selective line broadening due to rotation about the C–N bond becomes important. The multiplets at 320 and 330 K show broadening of the *outer* lines and this highly unusual effect proves that the two h.f.s. are of opposite signs. The second h.f.s. becomes 0 at *ca.* 330 K and above this temperature the multiplet evolves into a triplet. The final fast exchange limit is a 1:2:1 triplet and although this situation could not be achieved because of sample boiling and decomposition, the broadened central line of the

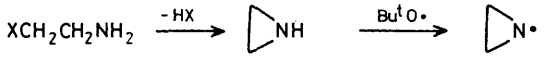
Table 3. E.s.r. parameters for aza-allyl radicals

Radical	Temp. (K)	H.f.s. (G) H^{1anti}	H^{1syn}	H^2	$H(D)^{3anti}$	N
 (6a)	206	17.75	16.85	3.05	12.25	6.75
 (6b)	206	17.65	16.75	2.85	11.60	6.60
	206	17.75	16.85	3.05	(2.05)[b]	6.75
 (7)	250	19.4	18.0			6.1

[a] *syn* Conformer too weak for analysis. [b] Deuterium h.f.s. [c] Allyl h.f.s.[26] $a(H^{1anti})$ 14.8, $a(H^{1syn})$ 14.0, $a(H^2)$ 4.16. [d] From ref. 30.

triplet is clearly visible at 369 K (Figure). Spectra were simulated using a two-jump model with the two $a(NH_2)$ obtained by extrapolation of values measured at lower temperatures. The Figure shows the satisfactory correspondence which was achieved.

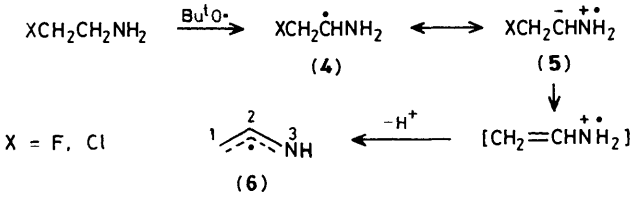
The photochemical reaction of 1-amino-2-fluoroethane with di-t-butyl peroxide in hydrocarbon solvents gave an e.s.r. spectrum which showed two radicals in the temperature range 160—290 K.[23] Their concentration ratio was *ca.* 2.5 at 262 K. No spectra were obtained in the absence of peroxide. Computer simulations gave good fits for two radicals each showing h.f.s. from four non-equivalent nuclei with $S = \frac{1}{2}$ and a nitrogen atom (Table 3). The same two radicals were detected when 2-chloroethylamine was used, but the concentration ratio was *ca.* 1.0 at 262 K. From these observations it follows that the two radicals are not aminoalkyls and that they very probably do not contain halogen atoms. The reaction products, which were t-butyl alcohol, an intractable polymer, and $FCH_2CH_2\overset{+}{N}H_3\bar{F}$ or, in the case of the chloroamine, $ClCH_2CH_2\overset{+}{N}H_3\bar{Cl}$, indicate a dehydrohalogenation step. Both the 2-halogenoamines dehydrohalogenate to give aziridine in the presence of base[24] and therefore the possibility that the reaction involved H-abstraction from aziridine was considered. Danen showed, however, that t-butoxyl radicals abstract the amino hydrogen



(3)

from aziridine to give 1-aziridinyl radicals (**3**) having e.s.r. parameters [a(4H) 30.7, a(N) 12.5 G][25] which are quite different from those observed here.

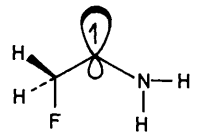
By analogy with other amines the first step in the reaction will be hydrogen abstraction at C_α to give 1-amino-2-halogenoalkyl radicals (**4**). The solution is quite polar because of the presence of the amine and, after the start of the reaction, of t-butyl alcohol, and the dipolar form (**5**) will make a significant contribution. Loss of halide from (**5**) either followed by proton



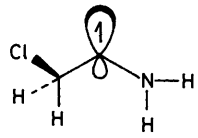
loss or concerted with proton loss will give 1-aza-allyl radicals (**6**). We assign the more intense spectrum to the *anti*- (**6a**) and the minor spectrum to the *syn*-conformer (**6b**). The reaction with $FCH_2CH_2ND_2$ gave a weak spectrum containing one deuterium [a(D) 2.05 G] which corresponded to the 12.25 G hydrogen h.f.s. of the major conformer and hence this must be the hydrogen attached to nitrogen. In allyl radicals[26] *anti*-hydrogens have larger h.f.s. and the complete assignments shown in Table 3 were made with the assumption that this rule would apply for aza-allyl radicals.

At first sight it is surprising that the monohalogenoamines dehydrohalogenate, while the 2,2,2-trifluoro derivative does not. However, Koch and his co-workers have shown from reactions of alkoxide with fluoroalkenes that F^- is a poorer leaving group when it comes from CF_3 in a carbanion than when it comes from a less highly fluorinated group.[27,28] Results on hydrogen fluoride elimination from anions of the compounds in the series $ArCH_2CH_xF_{3-x}$ show a similar trend.[29] The greater rate of fluoride loss from the monofluorocarbanions (**5**) as compared with the trifluoro analogue is in agreement with these precedents.

1-Aza-allyl radicals have not been observed previously, although the related 4,4-dimethyloxazolinylcarbinyl radicals (**7**) have been reported.[30] The good correspondence of the h.f.s. of radical (**7**) with those of the two radicals observed in this work is good evidence that they have been correctly identified. The formation of a higher ratio of *anti* to *syn* conformers from the 2-fluoroamine compared with the 2-chloroamine can be rationalised by examination of the conformations of the precursor radicals (**4**). In the preferred conformation of the 2-fluoroethyl radical the fluorine atom is in the nodal plane of the *p*-orbital containing the unpaired electron (SOMO) whereas in the preferred conformation of the 2-chloroethyl radical the chlorine atom eclipses the SOMO.[31] By analogy the preferred conformations of the 1-amino-2-fluoro- and -2-chloroethyl radicals will be (**8**) and (**9**) respectively.[23] Loss of HF from (**8**) to give the



(**8**)



(**9**)

anti-1-aza-allyl radical (**6a**) is stereoelectronically favoured whereas in (**9**) HCl loss can occur almost equally readily to give (**6a** or **b**).

We carried out semi-empirical SCF MO calculations for (**6a** and **b**) using the UHF versions of the MINDO/3 and MNDO methods.[32,33] The heats of formation of the *anti*-conformer (**6a**) were 34.9 and 35.4 kcal mol^{-1} calculated by the two methods respectively and 36.2 and 35.9 kcal mol^{-1} for the *syn*-conformer (**6b**). Thus, as expected, the *anti* conformer is predicted to be lower in energy by *ca.* 1 kcal mol^{-1}. Both methods predicted the two radicals to be planar, including the nitrogen atom, with the CCN angle greater in the *syn*-conformer. The optimum geometries from the MINDO/3 and MNDO calculations were used in INDO calculations[34] to compute the spin densities and h.f.s. Both geometries led to h.f.s. of about the same magnitude for the hydrogens at the C and N termini of the radicals. This disagrees with the experimental results (Table 3) which show the hydrogen h.f.s. at the C terminus to be greater than those in the allyl radical and the hydrogen h.f.s. at the nitrogen terminus to be smaller. Dannenberg and Tanaka recently examined 1-aza-allyl radicals using the MNDO method including configuration interaction.[35] These more sophisticated calculations predicted that the unpaired electron would be more localised on the C-terminus with significant double-bond character in the C=N bond. This is in good agreement with the experimental spin density distribution. INDO calculations using the C–C and C–N bond lengths found by Dannenberg and Tanaka (1.436 and 1.298 Å respectively)[35] gave satisfactory agreement with experiment; see Table 3.

Internal rotation about the partial C–N bond would interconvert (**6a** and **b**). Internal rotation about the partial C–C double bond would interconvert the *syn*- and *anti*-hydrogens on C(1), but would leave the two conformers distinct. Because the spin density is higher at the C terminus the rotation about the C–C bond would be expected to have the lower barrier. The MINDO/3 calculations predicted barriers of 6.5 and 8.6 kcal mol^{-1} for C–C and C–N rotation [(**6a**) to (**6b**)] respectively. The e.s.r. spectra were examined up to 300 K above which the signals became too weak for observation. At this temperature the [(**6a**)]/[(**6b**)] ratio was essentially the same as at 262 K and no sign of exchange broadening could be discerned. If a 'normal' pre-exponential factor of 10^{13} s^{-1} is assumed it follows that the rotation barriers in (**6**) must be > 8 kcal mol^{-1}.

Hydrogen Abstraction from Amino Acid Esters.—Amino acid esters are sufficiently soluble in hydrocarbon solvents for the photochemical reaction with di-t-butyl peroxide to be examined by e.s.r. spectroscopy. The only detectable radicals were again those produced by H-abstraction at C_α. The e.s.r. h.f.s. from the methyl and t-butyl esters of glycine and the t-butyl ester of alanine are in Table 1. The h.f.s. of the two non-equivalent amino hydrogens *decreased* in magnitude with increase in temperature, suggesting that they are negative in sign. Only the $Bu^tO_2C\dot{C}HNH_2$ radical gave a spectrum sufficiently intense for the exchange broadening to be followed in the range 400—470 K. Coalescence occurred at *ca.* 470 K and this was the maximum temperature at which radicals could be studied because of sample boiling and decomposition. Simulations were restricted to the region below coalescence, but quite good fits were achieved and the calculated barrier is in Table 2. The h.f.s. of the glycine ester radicals are similar to those of $H_2N\dot{C}HCOOH$ observed in aqueous solution.[4,13]

Rotation Barriers and Stabilisation Energies of Substituted Aminoalkyl Radicals.—Arrhenius parameters for internal rotation about the C–N bond in substituted aminoalkyl radicals are given in Table 2. In each case the pre-exponential factor is close to the 'normal' value of 10^{13} s^{-1} and this is good evidence of the reliability of the results. The rotation barriers, E_α, in the alkyl-substituted radicals are all identical to within the experimental error. The magnitude of the barrier (*ca.* 7.5 kcal mol^{-1}) is large in comparison with analogous C–C bond rotation barriers, but this is the expected consequence of spin delocalisation onto nitrogen,[17,20] and indicates significant stabilisation in aminoalkyl radicals. The barrier is evidently unaffected by the bulk of the substituent, and a barrier of *ca.* 7.5 kcal mol^{-1} can be postulated for the aminomethyl radical $^{\bullet}CH_2NH_2$ (for which exchange broadening does not occur).

The rotation barriers are related to the radical stabilisation energies, $SE^{ESR}(R^{\bullet})$, by equation (1)[16] where $SE^{ESR}(S^{\bullet})$

$$E_\alpha = V_2 + SE^{ESR}(R^{\bullet}) - SE^{ESR}(S^{\bullet}) \quad (1)$$

represents the stabilisation energy of the restricted radical formed in the transition state (**2**), and V_2 is the barrier to rotation about the *single* C–N bond in the absence of delocalisation. The V_2 values are not experimentally accessible but are small and probably[16,36] $\leqslant$ 1 kcal mol^{-1}. In the aminomethyl radical $SE^{ESR}(S^{\bullet})$ is 0 and hence $SE^{ESR}(^{\bullet}CH_2NH_2)$ = 6.5 kcal mol^{-1}. This is quite close to the SE found from the difference in $DH°(H_2NCH_2–H)$ (93 kcal mol^{-1}),[37] and $DH°$ for a primary C–H bond (98 kcal mol^{-1}) which gives $SE(^{\bullet}CH_2NH_2)$ 5 kcal mol^{-1}, but somewhat smaller than the $SE(^{\bullet}CH_2NH_2)$ value of 10 kcal mol^{-1} found by mass spectrometry.[17]

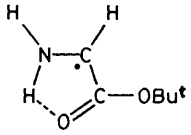
We showed previously that there is a linear correlation between the C–H bond dissociation energies in molecules of the type RCH_2–H and the corresponding barriers to rotation about the CH_2–R bonds, *i.e.* equation (2).[38] Use of this expression

$$DH°(RCH_2–H) \text{ kcal mol}^{-1} = 97.7 - 0.75E_\alpha \quad (2)$$

with the 7.5 kcal mol^{-1} barrier of the aminoethyl radical gives $DH°(H_2NCH_2–H)$ 92 kcal mol^{-1} which is in excellent agreement with the thermochemical value and shows that aminomethyl radicals fit well into this correlation.

The barrier for $CF_3\dot{C}HNH_2$ radicals, 10.9 kcal mol^{-1}, is particularly interesting because the radical is formally *destabilised* by the CF_3 group. For example, $DH°(CF_3CH_2–H)$ is[37] 106.7 kcal mol^{-1} which implies that the $CF_3CH_2^{\bullet}$ radical is destabilised, relative to secondary radicals, by 8.7 kcal mol^{-1}. Our experiment shows that the CF_3 and NH_2 groups, working in concert, cause an increase in the C–N barrier relative to aminoethyl radicals. It follows that either the ground-state energy must be lowered by the presence of the two substituents or the transition-state energy must be increased. It is likely that the latter explanation is correct because in the transition state (**2**) the unpaired electron is restricted to the $CHCF_3$ moiety with consequent destabilisation.

The rotation barriers found for the aminocyanomethyl, aminopropynyl, and (butoxycarbonyl)aminoethyl radicals provide *prima facie* evidence for a small captodative (CD) stabilisation.[21,39–41] The barriers of these radicals are all significantly greater than those of the aminoalkyl radicals. However, it is extremely difficult to derive quantitative SEs for disubstituted radicals.[16] The effect of two substituents is normally less than additive; for example, SE(pentadienyl) is *ca.* 5 kcal mol^{-1} less than twice SE(allyl), and $SE(Ph_2CH^{\bullet})$ is *ca.* 10 kcal mol^{-1} less than twice SE(benzyl).[16] In the case of the CD substituted radicals in Table 2 the stabilisation due to each individual substituent is not known accurately enough to quantify the effect. For $Bu^tOCO\dot{C}HNH_2$ radicals the Bu^tOCO stabilisation is not known. Thermochemical studies of related radicals have suggested negligible stabilisation[37,42] whereas e.s.r. studies of $^{\bullet}CH_2COOR$ radicals[43] have indicated barriers as high as 9 kcal mol^{-1}. Thus the sum of the SEs due to the two groups could be anywhere from 6.5 to 15.5 kcal mol^{-1}. This particular radical has the further complication that the rotational barrier could be increased by intramolecular hydrogen bonding (**10**). Thermochemical estimates[37] of the SE



(**10**)

of the cyanomethyl radical range around 5 kcal mol^{-1}. Thus the sum of the stabilisation due to the CN and NH_2 groups in the $NC\dot{C}HNH_2$ radical is *ca.* 11.5 kcal mol^{-1}, which is rather close to the measured barrier of 11 kcal mol^{-1} (Table 2). Because the effects of the two substituents are normally less than additive this result is also consistent with an additional C–D stabilisation. The effect cannot be properly quantified until the stabilisation energies of a wider range of radicals become available.

Experimental

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

Methylamine, ethylamine, n-propylamine, isobutylamine, and neopentylamine were commercial materials, used without further purification. 2,2,2-Trifluoroethylamine, 2-fluoroethylamine, and 2-chloroethylamine were obtained as the hydrochlorides. The free fluoro-amines were liberated by dry distillation of the hydrochloride with NaOH. 2-Chloroethylamine was prepared in t-butylbenzene by bubbling NH_3 gas through a suspension of the hydrochloride and filtering off the precipitate of NH_4Cl. The deuteriated amines $FCH_2CH_2ND_2$ and $ClCH_2CH_2ND_2$ were made by stirring the amines with an excess of D_2O.

Reaction of 2-Fluoroethylamine with Di-t-butyl Peroxide.—The amine (2.1 mmol) and di-t-butyl peroxide (2.1 mmol) in hexadecane (1 ml) were placed in a quartz tube, degassed, and photolysed with light from a 500 W medium pressure mercury arc for 21 h at ambient temperature. The volatiles were distilled out using a high vacuum line and analysed by g.l.c. which showed the presence of t-butyl alcohol, in addition to unchanged starting materials. The experiment was repeated in n-pentane as solvent with photolysis for 1.5 h and all volatiles were blown off in a stream of nitrogen. The residue was extracted with D_2O leaving a sticky polymer. The ^1H n.m.r. spectrum showed four double doublets (J_F 47 and 28 Hz) and the ^{19}F spectrum showed signals at δ 225 (dd, *J* 47, 28 Hz), 121.7 (s), and *ca.* 210 (br) p.p.m. (relative to CCl_3F). Thus the main products are Bu^tOH, $FCH_2CH_2NH_3^+F^-$, and polymer.

Reaction of 2-Chloroethylamine with Di-t-butyl Peroxide.—To 1 cm^3 of a 20% solution of $ClCH_2CH_2NH_2$ in t-butylbenzene was added di-t-butyl peroxide (0.4 ml). The mixture was placed in a quartz tube, degassed, and then photolysed with light from a 500 W medium pressure mercury arc for 3 h at ambient temperature. The volatiles were distilled out using a vacuum line and shown to contain Bu^tOH together with unchanged starting material by g.l.c. analysis. The residue after distillation was extracted with D_2O and the ^1H n.m.r. spectrum of the resulting solution was identical to that of authentic $ClCH_2CH_2NH_3^+Cl$ together with some broad (unidentified) peaks.

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References

1 H. Taniguchi, K. Fukui, S. Ohnishi, H. Hatano, H. Hasegawa, and T. Maruyama, *J. Phys. Chem.*, 1968, **72**, 1926.
2 R. Poupko, B. L. S. Iver, and A. Lowenstein, *Chem. Commun.*, 1968, 453.
3 P. Smith, W. M. Fox, D. J. McGinty, and R. D. Stevens, *Can. J. Chem.*, 1970, **48**, 480.
4 P. Neta and R. W. Fessenden, *J. Phys. Chem.*, 1971, **75**, 738.
5 R. O. C. Norman and N. H. Anderson, *J. Chem. Soc. B*, 1971, 993.
6 G. G. Jayson, G. Scholes, and J. J. Weiss, *J. Chem. Soc.*, 1955, 2594.
7 P. J. Wagner, *Top. Curr. Chem.*, 1976, **66**, 1.
8 Y. Maeda and K. U. Ingold, *J. Am. Chem. Soc.*, 1980, **102**, 328.
9 D. Griller, J. A. Howard, P. R. Marriot, and J. C. Scaiano, *J. Am. Chem. Soc.*, 1981, **103**, 619.
10 C. J. Easton and M. P. Hay, *J. Chem. Soc., Chem. Commun.*, 1986, 55.
11 A. Hedberg and A. Ehrenberg, *J. Chem. Phys.*, 1968, **48**, 4822.
12 M. A. Collins and D. H. Whiffen, *Mol. Phys.*, 1966, **10**, 317.
13 H. Paul and H. Fischer, *Helv. Chim. Acta*, 1971, **54**, 485.
14 J. C. Scaiano, *J. Phys. Chem.*, 1981, **85**, 2851.
15 M. J. S. Dewar, M. A. Fox, and D. J. Nelson, *J. Organomet. Chem.*, 1980, **185**, 157.
16 J. C. Walton, *Rev. Chem. Intermed.*, 1984, **5**, 249.
17 D. Griller and F. P. Lossing, *J. Am. Chem. Soc.*, 1981, **103**, 1586.
18 M. V. Encina and E. Lissi, *Int. J. Chem. Kinet.*, 1978, **10**, 653.
19 K. A. McLauchlan and A. J. D. Ritchie, *J. Chem. Soc., Perkin Trans. 2*, 1984, 275.
20 D. Griller, D. C. Nonhebel, and J. C. Walton, *J. Chem. Soc., Perkin Trans. 2*, 1983, 1373.

21 I. MacInnes, J. C. Walton, and D. C. Nonhebel, *J. Chem. Soc., Chem. Commun.*, 1985, 712.
22 J. Heinzer, Quantum Chemistry Program Exchange, No. 209, University of Indiana, 1972.
23 I. MacInnes and J. C. Walton, *J. Chem. Soc., Chem. Commun.*, 1986, 1604.
24 P. L. Levins and Z. B. Papanastassiou, *J. Am. Chem. Soc.*, 1965, **87**, 826.
25 W. C. Danen and T. T. Kensler, *Tetrahedron Lett.*, 1971, 2247.
26 J. K. Kochi and P. J. Krusic, *J. Am. Chem. Soc.*, 1968, **90**, 7157; A. L. J. Beckwith and R. O. C. Norman, *J. Chem. Soc. B*, 1969, 400.
27 H. F. Koch and A. J. Kielbania, *J. Am. Chem. Soc.*, 1970, **92**, 729.
28 H. F. Koch, *Acc. Chem. Res.*, 1984, **17**, 137.
29 C. H. DePuy and A. L. Schaltz, *J. Org. Chem.*, 1974, **39**, 878.
30 D. C. Nonhebel and J. C. Walton, *Tetrahedron*, 1985, **41**, 1763.
31 J. K. Kochi, *Adv. Free Radical Chem.*, 1975, **5**, 189.
32 R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, 1975, **97**, 1285.
33 J. J. P. Stewart, Quantum Chemistry Program Exchange, No. 455, University of Indiana, 1983.
34 J. A. Pople and D. L. Beveridge, 'Approximate Molecular Orbital Theory,' McGraw-Hill, New York, 1970.
35 J. J. Dannenberg and K. Tanaka, *J. Am. Chem. Soc.*, 1985, **107**, 671.
36 H.-G. Korth, H. Trill, and R. Sustmann, *J. Am. Chem. Soc.*, 1981, **103**, 4483.
37 D. F. McMillen and D. M. Golden, *Annu. Rev. Phys. Chem.*, 1982, **33**, 493.
38 D. C. Nonhebel and J. C. Walton, *J. Chem. Soc., Chem. Commun.*, 1984, 731.
39 H. G. Viehe, R. Merenyi, L. Stella, and Z. Janousek, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 917.
40 A. de Mesmaeker, L. Vertommen, R. Merenyi, and H. G. Viehe, *Tetrahedron Lett.*, 1982, **23, 69.**
41 S. Mignani, M. Beaujean, Z. Janousek, R. Merenyi, and H. G. Viehe, *Tetrahedron*, 1981, **37**, 111.
42 K. D. King, D. M. Golden, and S. W. Benson, *J. Am. Chem. Soc.*, 1970, **92**, 5541.
43 W. Lung-Min and H. Fischer, *Helv. Chim. Acta*, 1983, **66**, 138.

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