An Electron Spin Resonance Study of Aminoallyl, Aminopropynyl, and Aminocyanomethyl Radicals

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E.s.r. spectra have been obtained for series of *N*-alkyl-substituted aminoallyl and aminopropynyl radicals and for aminocyanomethyl radicals. The hyperfine splittings indicate that considerable spin density is delocalised on to the NR_2 group. The amino group is a more effective acceptor of spin than alkyl-, halogen, hydroxy- or alkoxy-substituents and only slightly less effective than the vinyl substituent. The barrier to rotation about the C–N bond in aminopropynyl radicals was calculated to be 44 ± 5 kJ mol^{-1} from the temperature dependence of the e.s.r. line widths, and this leads to a value of 107 kJ mol^{-1} for the methane-based stabilisation energy of the radical. The geometries, enthalpies of formation, and stabilisation energies of the series of *N*-alkyl-substituted allyl and propynyl radicals were also investigated by semi-empirical SCF MO methods.

Recent studies by mass spectrometry[1] have shown that α-aminoalkyl radicals, ($R_2NCH_2^{\bullet}$; R = H or alkyl), have remarkably high stabilisation energies, which increase with increasing *N*-alkylation. For example, the methane-based stabilisation energies[2] of $H_2NCH_2^{\bullet}$ and $Me_2NCH_2^{\bullet}$ were found to be 42 and 84 kJ mol^{-1}, respectively.[1] Electron spin resonance (e.s.r.) spectra of α-aminoalkyl radicals[3] offer qualitative support for these unusually high values, since they show that there is extensive delocalisation of the unpaired electron on to the nitrogen atom. Nevertheless, the magnitudes of these stabilisation energies and their variation with *N*-alkylation remain controversial since they are at variance with earlier measurements[4,5] and theoretical calculations.[6]

In order to check the validity of these conclusions, we have undertaken an e.s.r. study of aminoallyl, ($R_2N\dot{C}H{-}CH{=}CH_2$), aminopropynyl ($R_2N\dot{C}H{-}C{\equiv}CH$), and aminocyanomethyl radicals.[7] Aminopropynyl radicals are of especial interest since they are thought to be intermediates in enzyme deactivation by acetylenic amines.[7] In these cases the carbon–carbon and carbon–nitrogen multiple bonds can compete with the nitrogen atoms for delocalisation of the unpaired electron. Since the stabilising properties of the carbon–carbon moieties are well characterised it seemed probable that such a study would remove any doubts about the stabilising power of the R_2N group and its variation with *N*-alkylation. Moreover, it was further possible that the presence of the carbon–carbon multiple bonds would reduce the torsional barrier about the C–N bond so that the onset of this rotation could be detected in e.s.r. experiments. Such measurements can be used to determine radical stabilisation energies.[8-10] In a preliminary communication[11] we reported the e.s.r. spectrum of the aminopropynyl radical and its stabilisation energy. Despite the great interest in allyl and propynyl radicals as the simplest acyclic systems containing three π-electrons there do not appear to be any other reports on the e.s.r. spectra of aminoallyl or aminopropynyl radicals.

Results

Aminoallyl (1) and aminopropynyl (2) radicals were generated in the cavity of the e.s.r. spectrometer by hydrogen abstraction from 3-aminopropenes and 3-aminopropynes by t-butoxyl radicals. Cyclopropane was used as solvent for low-temperature work and neat di-t-butyl peroxide or t-butylbenzene for temperatures above *ca.* 240 K. From each of the amines examined a single allyl or propynyl radical was observed, *i.e.* the allylic or propynylic hydrogens were preferentially abstracted with no detectable attack on the amino hydrogens or the alkyl groups. The spectrum of the aminoallyl radical (1a) at 240 K is shown in Figure 1 and the e.s.r. parameters are given in Table 1 along with the results for methylaminoallyl (1b) and t-butylaminoallyl (1c) radicals. The spectra all showed variations with temperature but were too weak to enable these to be charted accurately. Hydrogen abstraction from 3-(dimethylamino)propene gave a radical with a very large number of e.s.r. lines. The spectrum had a width of about 6.3 mT and we attribute it to the dimethylaminoallyl radical (1d). However, the weakness of individual lines precluded analysis.

The e.s.r. spectra of aminopropynyl radicals (2a) (Figure 2) underwent substantial change with temperature. The 3-aminopropyne crystallised out of hydrocarbon solvents at $T < ca.$ 220 K and the spectrum was examined from this point up to 370 K. The spectra of t-butylaminopropynyl radicals (2c) and dimethylaminopropynyl radicals (2d) were also examined and the e.s.r. parameters are given in Table 2. The spectrum of the t-butyl-substituted radical (2c) was essentially invariant with temperature. The dimethyl-substituted radical (2d) could only be observed at low temperatures (*ca.* 160 K); individual lines were too weak for unambiguous analysis at higher temperatures. The aminocyanomethyl radical, $H_2N\dot{C}HCN$, was generated by hydrogen abstraction from aminoacetonitrile in acetonitrile solvent and the e.s.r. spectra were studied in the temperature range 230—320 K. The hyperfine splittings (h.f.s.) are recorded in Table 2.

Discussion

The h.f.s. were assigned to specific hydrogens by comparison with other allyl[8,12-17] and propynyl[13,18-20] radicals. There are two possible conformations of the aminoallyl radicals in which the amino group occupies an *exo* or an *endo* position. Both conformers have been observed at higher temperatures for some other substituted allyl radicals.[16,17,21] Only one radical was detected from each aminopropene in this study; probably because of the weakness and complexity of the spectra at higher temperatures or alternatively because steric effects favour one conformer. We have assumed that the radical

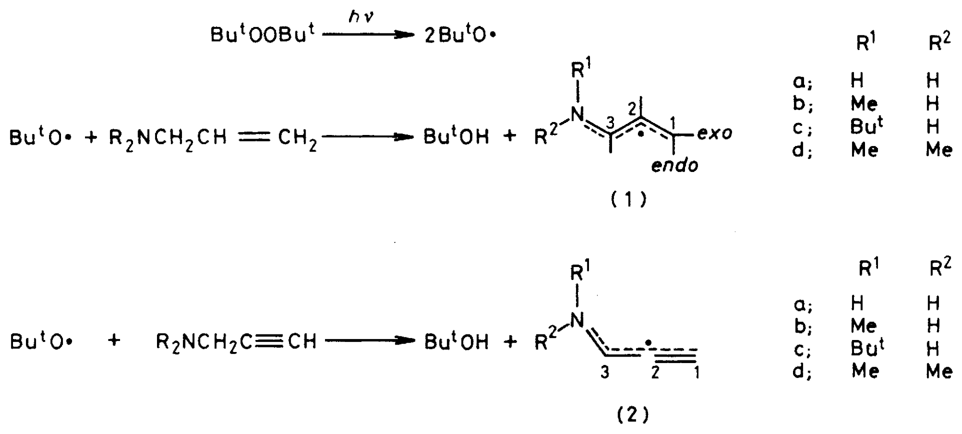


Table 1. E.s.r. h.f.s. for aminoallyl radicals

Radical	T/K	H.f.s. (mT)						
		H_1*exo*	H_1*endo*	H^2	H^3	N	H/CH_3^N	H/CH_3^N
Allyl[a]	143	1.48	1.39	0.41				
(1a)	240	1.25	1.21	0.24	1.16	0.33	0.04	<0.02
(1b)	137	1.17	1.12	0.20	1.07	0.37	0.20 (H)	0.37 (CH_3)
(1c)	148	1.17	1.17	0.19	1.15	0.40	0.17 (H)	

[a] Data from ref. 13.

Table 2. E.s.r. h.f.s. for aminopropynyl and aminocyanomethyl radicals

Radical	T/K	H.f.s. (mT)					
		H^1	H^3	N	H/R^N	H/R^N	N^{CN}
Propynyl[a]	151	1.27	1.89				
(2a)	370	0.81	1.47	0.50	0.16	0.16	
(2c)	137	0.80	1.37	0.59	0.23 (H)	0.025 $(CH_3)_3C$	
(2d)	137	0.80	1.36	0.70	0.45 (CH_3)	0.37 (CH_3)	
(6)	227		1.49	0.62	0.34	0.34	0.30

[a] Data from ref. 13.

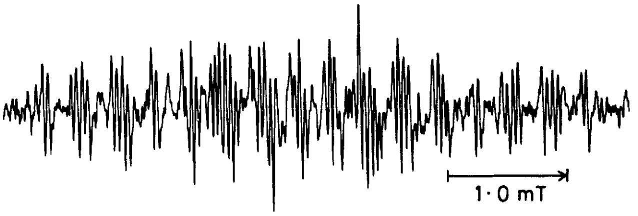


Figure 1. 9.4 GHz e.s.r. spectrum of aminoallyl radicals (1a) in neat di-t-butyl peroxide at 240 K

observed is the thermodynamically more stable *exo* conformer in each case.

Tables 1 and 2 show that the h.f.s. of all the hydrogens of the allyl and propynyl moieties of the amino-substituted radicals are considerably reduced from their values in the parent allyl and propynyl radicals. A methyl-[13,22] or a chloro-[23] substituent has virtually no effect on the h.f.s. of the remaining hydrogens, and hydroxy-[21] and methoxy-[16] substituents have only a small effect (<0.08 mT for all hydrogens). This evidence, together with the relatively high h.f.s. of the nitrogen atoms and their associated hydrogens [even the hydrogens of the Buᵗ group are resolved in (2c)] indicates a high degree of spin delocalisation on to the amino groups. In fact the h.f.s. of the allyl hydrogens in (1) are similar in magnitude to those of pentadienyl radicals[9] (which may be thought of as allyl radicals substituted by a vinyl group). Similarly, the h.f.s. of the propynyl hydrogens in radicals (2) are comparable with those of pent-1-en-4-ynyl radicals[24] (which may be thought of as propynyl radicals substituted by a vinyl group). Thus the amino group appears to be only slightly less effective than the vinyl group at delocalising spin.

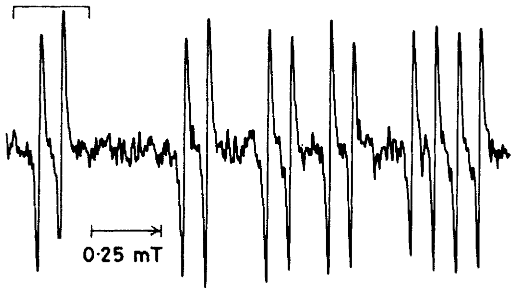


Figure 2. Low-field half of the 9.4 GHz e.s.r. spectrum of aminopropynyl radicals (2a) in neat di-t-butyl peroxide at 280 K. The bracketed region is shown with an expanded scale in Figure 3

Tables 1 and 2 also show that there is an increase in a(N)

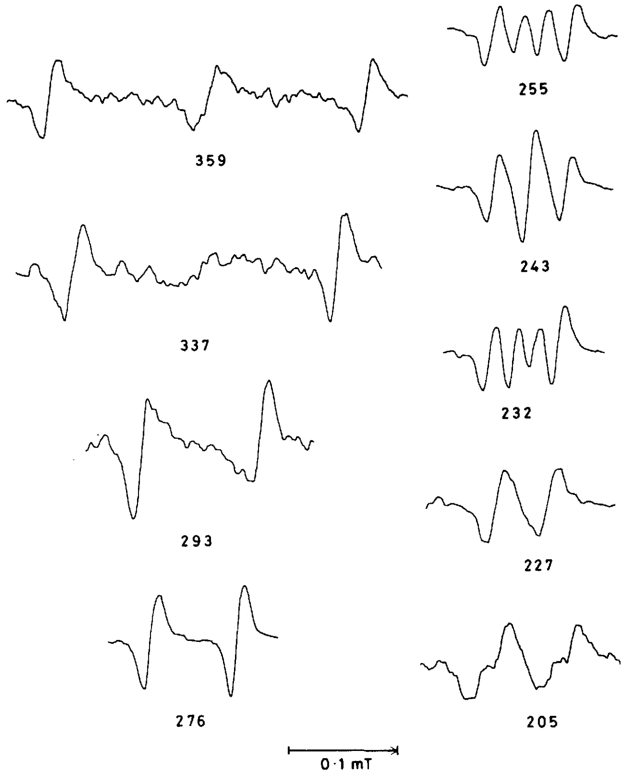
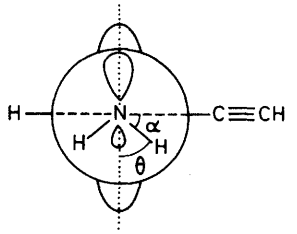


Figure 3. Low-field multiplet (see Figure 2) from the e.s.r. spectrum of radical (2a) at various temperatures as indicated (K)

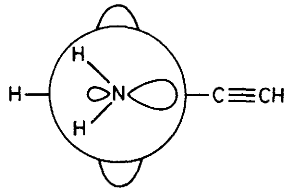
with increasing *N*-alkylation for both series of radicals. There is also a parallel decrease in the h.f.s. of the allyl and propynyl hydrogens. It appears therefore that alkyl substitution enhances the ability of the amino group to accept spin density and this supports the contention [1] that *N*-alkyl groups increase the stabilisation energies of aminoalkyl radicals.

Table 3. Rate constants for rotation about the C–N bond, obtained using $a_1 - a_2 = 0.05$ mT, measured unbroadened line widths, and observed signal intensities

T/K	319	329	339	339	349	359	369
$10^6 k$/ s^{-1}	2.98	4.29	6.17	5.26	12.24	18.0	24.9



(3)



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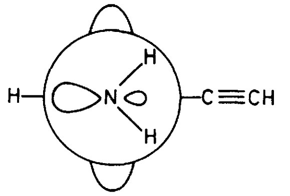


(5)

The majority of the radicals could not be studied over a range of temperatures because of the weak signal intensities. However, the aminopropynyl (2a) and aminocyanomethyl radicals (6) had sufficiently intense spectra to allow rotation about the C–N bond (and hence the radical stabilisation energies) to be investigated. The h.f.s. of the propynyl hydrogens and the nitrogen atom of (2a) were virtually independent of temperature ($\delta a/\delta T \leqslant 0.4\ \mu T\ K^{-1}$), but the h.f.s. of the amino hydrogens showed a remarkable evolution with temperature (Figure 3). In the region 205—280 K, H(1) and H(2) had different h.f.s. showing that there was restricted rotation about the C–N bond. Above *ca.* 280 K rotation about the C–N bond became significant on the e.s.r. time scale, as was shown by the selective line broadening (see Figure 3). By 300 K, H(1) and H(2) were magnetically equivalent. Above the coalescence temperature relaxation matrix theory can be applied to the rate process. Assuming Lorentzian line shapes, and that the signal heights are inversely proportional to the squares of the line widths, ΔH_{pp}, the first-order rate constant is given by equation (1),[25] where a_1 and a_2 are the h.f.s. of the inequivalent H(1) and H(2) in the limit of slow exchange, $(\Delta H_{pp})_u$ is the width of the unbroadened lines in mT, and I_u and I_b are the intensities of the theoretical unbroadened and observed broadened lines, respectively. At the

$$k(\mathrm{s}^{-1}) = 2.5 \times 10^7[(a_1 - a_2)^2/(\Delta H_{pp})_u][(I_u/I_b)^{\frac{1}{2}} - 1]^{-1} \quad (1)$$

lowest temperature at which observations could be made (205 K) $a_1 - a_2 = 0.05$ mT. Using this value, together with the measured unbroadened line widths and the observed signal intensities the rate constants shown in Table 3 for rotation about the C–N bond were obtained. An Arrhenius plot of the data gave $\log(A/\mathrm{s}^{-1}) = 13.7 \pm 0.7$, $E = 44 \pm 5$ kJ mol^{-1}, with a correlation coefficient of 0.985. The *A*-factor is normal for a process of this type; the activation energy is independent of the value taken for $a_1 - a_2$.

The triplet h.f.s. from H(1) and H(2) decreases markedly with decreasing temperature down to *ca.* 280 K. Below this temperature the splitting pattern undergoes the following sequence of changes with decreasing temperature: d ⟶ dd ⟶ t ⟶ dd ⟶ d ⟶ dd (partly resolved) (d = doublet, dd = double doublet, and t = triplet) (see Figure 3). The h.f.s. of the amino hydrogens depend on the dihedral angle, θ, between the $\dot{C}$ $2p_z$ orbital and the N–H bond, and this dependence can be represented by $a(\mathrm{H}_\beta) = A + B\cos^2\theta$. For radical (2a) certain θ values are preferred but the populations of different conformers vary with temperature. Three limiting conformations (3), (4), and (5) may be considered. For (3) the amino hydrogens would be non-equivalent with small h.f.s. at low temperatures that should increase at higher temperatures, in agreement with the experimental observations. Neither conformation (4) nor (5) can fit the observations. The changes in the splitting pattern of the amino hydrogens can be explained in the following manner. At the lowest temperature (205 K) H(1) and H(2) are non-equivalent with negative h.f.s. thus giving a dd splitting. The two hydrogens experience slightly different average environments and, as the temperature increases, torsional motions about the C–N bond will result in more positive spin density reaching

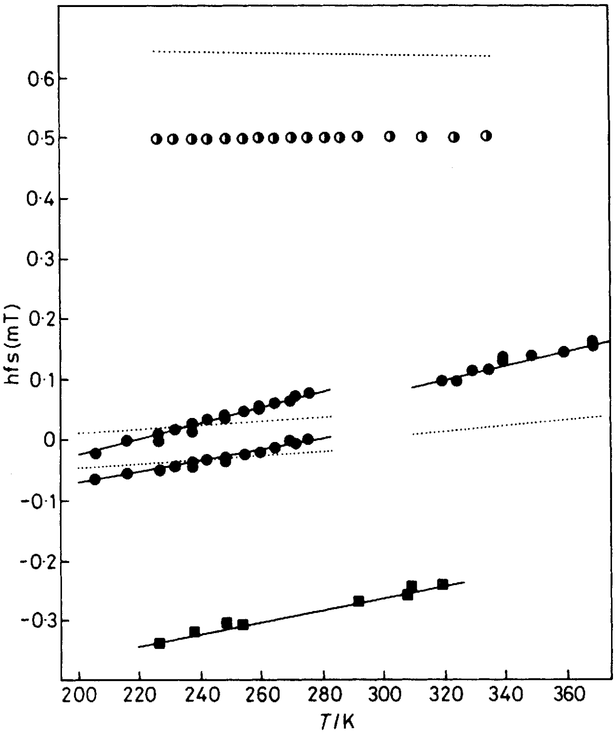


Figure 4. Temperature variation of the h.f.s. of aminopropynyl radicals (2a) and aminocyanomethyl radicals (6). Half-filled circles, experimental h.f.s. of nitrogen atom of (2a); filled circles, experimental h.f.s. of amino hydrogens of (2a); filled squares, experimental h.f.s. of amino hydrogens of (6); full lines calculated from equation (3) (see text); dotted lines, INDO calculations

the amino hydrogens by a hyperconjugative mechanism. Both h.f.s. increase so that at 227 K one becomes zero while the other is still negative and a doublet is obtained. At 232 K the dd pattern is due to two unequal h.f.s. of opposite sign, which become equal in magnitude (but opposite in sign) at 243 K, thus giving the triplet pattern. The positive h.f.s. continues to increase and the other also becomes less negative (*i.e.* decreases in magnitude) so that at 255 K a dd pattern is again obtained. At 276 K the second h.f.s. becomes zero and the pattern becomes a doublet from the single positive h.f.s. Above 280 K both h.f.s. are positive and increase in magnitude, but at the same time the rate of rotation about the C–N bond is such that selective line broadening occurs. At higher temperatures the rate of rotation becomes sufficiently fast that the two hydrogens experience the same average environment so that a triplet is obtained. This situation has not quite been reached at the highest accessible temperatures (see Figure 3). The variation in the h.f.s. of the two amino hydrogens with temperature, according to this explanation, is plotted in Figure 4.

Alternatively the temperature evolution of the amino hydrogen h.f.s. could be explained by a similar sequence of events but with the signs of the h.f.s. reversed. This is almost certainly incorrect because it disagrees with what is known about the signs and temperature dependencies of the h.f.s. of β-hydrogens in alkyl radicals.[26] Additionally, in the related hydroxymethyl radical, the h.f.s. of the hydroxy hydrogen is negative at low temperatures and decreases in magnitude as the temperature is raised.[27]

Rotation about the C–N bond in radical (3) is probably of the normal two-fold type with potential energy given by equation (2), where V_0 is the height of the barrier and θ^1 is the dihedral angle measured from the potential-energy minimum.

$$V = \tfrac{1}{2}V_0(1 - \cos 2\theta^1) \qquad (2)$$

Semi-empirical SCF MO calculations (see later) indicate that this is a reasonable approximation. The potential barrier to rotation about the C–N bond can be estimated by fitting the observed temperature dependence of the h.f.s. of the amino hydrogens with calculated values. A classical limit approach [26,28] was shown to give essentially the same results for a number of radicals as a more cumbersome quantum mechanical procedure.[26,29] We showed recently [30] that the classical limit approach leads to the expression for the h.f.s. of β-hydrogens shown in equation (3), where $I_1(\lambda)$ and $I_0(\lambda)$ are

$$\langle a(\mathrm{H}_\beta)\rangle = A + \tfrac{1}{2}B + \tfrac{1}{2}B\cos 2\theta_0\left[\frac{I_1(\lambda)}{I_0(\lambda)}\right] \qquad (3)$$

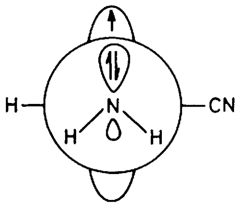
modified (hyperbolic) Bessel functions, $\lambda = V_0/kT$, and θ_0 is the value of θ at the potential minimum. A similar treatment has been given by Biddles *et al.*[31] The barrier height is determined by fitting equation (3) to the observed amino h.f.s. and varying A, B, and V_0 so as to get the best fit. If the aminopropynyl radical is pyramidal at nitrogen, and the MO calculations suggest it is (see later), then in the preferred conformation (3) θ_0 lies between 60 and 90°. However, the barrier to inversion at nitrogen will be similar to that of ammonia (24.8 kJ mol^{-1}),[32] or possibly somewhat less, and hence inversion will be rapid in comparison with internal rotation. The average value of θ_0 under these conditions will be 90°. In fact a good fit of the h.f.s. calculated by equation (3) to the experimental results cannot be obtained except with θ_0 values of 90° or close to this.

An excellent fit to the high-temperature points can be obtained by taking $A = -0.23$ mT, $B = 9.9$ mT, and $V_0 = 42$ kJ mol^{-1}. The low-temperature data can be fitted by taking $A = -0.265$ mT, $B = 12.0$ mT, $V_0 = 42$ kJ mol^{-1} for the upper curve and $A = -0.225$ mT, $B = 7.9$ mT, and $V_0 = 42$ kJ mol^{-1} for the lower curve (see Figure 4). The ' fits ' to the experimental points were somewhat ' soft ' and reasonable agreement could be obtained with slightly different values of the parameters. Unfortunately, the fits were not very sensitive to the value of V_0 but were sensitive to the value of B; good fits being unobtainable for B values much less than those quoted. The high-temperature parameters are close to the average of the low-temperature parameters, as would be expected. The A values seem reasonable in view of the negative amino hydrogen h.f.s. at low temperatures and V_0 is in good agreement with the activation energy derived from the line-broadening data. However, the B values are much greater than those obtained for alkyl [26,30] or hydroxymethyl radicals,[27] and are not supported by INDO calculations (see below). It is possible that internal rotation and inversion at nitrogen may be coupled so that a more elaborate potential function than equation (2) may be needed. In view of the uncertainties in θ_0 and B this method can only be regarded as giving order of magnitude estimates for V_0.

The h.f.s. of the amino hydrogens of aminocyanomethyl radicals (6) decreased in magnitude with increasing temperature (see Figure 4) but the two hydrogens remained equivalent throughout the accessible temperature range. This radical adopts conformation (6), which is similar to that of the aminopropynyl radical. The amino hydrogen h.f.s. became less negative with increasing temperature, but their average environments were sufficiently similar for them to remain spectroscopically equivalent even at the lowest temperatures. The temperature dependence of the amino hydrogen h.f.s.can be reproduced by equation (3) using $\theta_0 = 90°$, $A = -0.55$ mT, $B = 9.9$ mT, and $V_0 = 45$ kJ mol^{-1} (see Figure 4). The pro-

Table 4. Computed enthalpies of formation and stabilisation energies of aminoallyl and aminopropynyl radicals (kJ mol^{-1})

	ΔH_f (R$^\cdot$)			ΔH_f (RH)			E_s^{MeH}		
Radical	MINDO/3	MNDO	UMNDO	MINDO/3	MNDO	UMNDO	MINDO/3	MNDO	UMNDO
(1a)	115	131	91	44	49	56	132	76	117
(1b)	152	135	95	79	55	56	130	78	114
(1d)	237	161	121	153	75	74	119	72	105
(2a)	236	286	262	150	195	195	117	67	86
(2b)	275	289	289	190	203	214	118	72	78
(2d)	357	311	304	266	225	227	112	72	76



(6)

cedure is subject to the same uncertainties as in the preceding case, *i.e.* the unknown degree of pyramidality at nitrogen, the insensitivity of the fits to the value of V_0, and the unexpectedly high B value; thus the calculated barrier height can only be regarded as a rough estimate.

The high barriers to rotation about the C–N bonds in radicals (2a) and (6) confirm the conclusion drawn from the h.f.s., namely that there is appreciable overlap of the nitrogen orbital with the rest of the π-system. The measured barrier in (2a), *i.e.* 44 ± 5 kJ mol^{-1}, may be compared with the barrier to rotation in pent-1-en-4-ynyl radicals (48—49 kJ mol^{-1}). The similarity in the two barriers indicates that the NH_2 group is slightly less effective than the $-CH{=}CH_2$ group at delocalising spin. This also agrees very well with the deduction made from the comparison of the h.f.s. of the two radicals (*vide supra*). Similarly, the measured barrier in aminocyanomethyl radicals (45 kJ mol^{-1}) is quite close to that observed in cyanoallyl radicals (41 kJ mol^{-1}),[33] which again shows that $-NH_2$ and $-CH{=}CH_2$ are comparable in their ability to stabilise radicals by electron delocalisation.

In the transition state for rotation about the C–N bond the unpaired electron is confined to the propynyl unit for radical (2a) and the cyanomethyl unit for radical (6). The stabilisation energies of the amino radicals (2a) and (6) can be considered as being equal to the sum of the energy associated with the barrier to rotation plus the propynyl or cyanomethyl stabilisation energy.[9,10] Recent estimates of the methane-based stabilisation energy,[9,24] E_s^{MeH}, of propynyl radicals indicate [34,35] a value of 63 ± 9 kJ mol^{-1}. Thus the methane-based stabilisation energy of the aminopropynyl radical is 63 + 44 = 107 kJ mol^{-1}. The stabilisation energy of the α-aminomethyl radical is [1] 42 ± 8 kJ mol^{-1} and hence E_s^{MeH}(propynyl) + E_s^{MeH}(aminomethyl) = 105 kJ mol^{-1}. The measured E_s^{MeH} (aminopropynyl) is therefore approximately equal to the sum of the stabilisation energies associated with the two substituents.

The E_s^{MeH} value for cyanomethyl is [36,37] 50 ± 12 kJ mol^{-1} and hence E_s^{MeH}(aminocyanomethyl) = 50 + 45 = 95 kJ mol^{-1}. Therefore the stabilisation energy of this 'captodative' radical containing an electron-accepting and an electron-accepting and an electron-donating substituent is also equal, within the experimental error, to the sum of the stabilisation energies associated with the substituents, *i.e.* E_s^{MeH}(cyanomethyl) + E_s^{MeH}(aminomethyl) = 92 kJ mol^{-1}.

Semi-empirical SCF MO Calculations.—The optimum geometries and the corresponding enthalpies of formation, ΔH_f, of a number of the aminoallyl and aminopropynyl radicals were calculated using the MINDO/3 [38] and MNDO [39] methods of Dewar and his co-workers; the UHF version of the MNDO program, *i.e.* UMNDO,[40] was also employed. The E_s^{MeH} values of odd conjugated radicals, R$^\cdot$, can be calculated from the enthalpies of formation by means of equation (4).[2] The calculated values are shown in Table 4 for increasing

$$E_s^{MeH} = [\Delta H_f(CH_3^\cdot) - \Delta H_f(CH_4)] - [\Delta H_f(R^\cdot) - \Delta H_f(RH)] \quad (4)$$

N-alkylation in the two types of radicals. The calculations correctly predict greater stabilisation energies for the aminoallyl as compared with the aminopropynyl radicals. The calculated E_s^{MeH} values, by the three methods, for aminopropynyl radicals (2a) bracket the experimental value. The calculated enthalpies of formation increase with increasing *N*-alkylation for both series of radicals, but so do the ΔH_f values of the precursors RH. This leads to approximate cancellation in the E_s^{MeH} values with no well marked trend being observed. There are some serious discrepancies in the ΔH_f values calculated by the three methods and it is evident that the calculational errors are too great for a small increasing trend in the E_s^{MeH} values with increasing *N*-alkylation to be revealed.

The aminopropynyl radical (2a) was selected for more detailed study because of the more extensive experimental results. The optimum geometry predicted by the UMNDO calculations was: r(C≡C) = 1.21, r(C–C) = 1.39, and r(C–N) = 1.40 Å. The preferred conformation was predicted to be (3), in agreement with experiment, with a planar radical centre and a pyramidal nitrogen. The bond angles about the nitrogen atom were calculated to be close to tetrahedral and α, the angle between the N–H bonds and the plane containing the nitrogen and carbon atoms [see (3)] was found to be 30°. In radical (2a) the calculated C–N bond length was considerably shorter than that of 3-aminopropyne, for which r(C–N) = 1.47 Å was obtained. Thus theory agrees in assigning partial double bond character to the C–N bond. The barrier to rotation about the C–N bond was calculated to be 19 kJ mol^{-1}. Although this is considerably less than the experimental value, it is an additional indicator of the very significant delocalisation on to nitrogen. The barrier to inversion at nitrogen was calculated to be 15 kJ mol^{-1}, which is also probably lower than the true barrier (*cf.* the inversion barrier in NH_3).

Calculations were also carried out for radical (2a) using the INDO method of Pople and Beveridge.[41] The optimised r(C–C) was 1.41 Å and r(C–N) was 1.38 Å, in reasonable agreement with the UMNDO results. The INDO method also predicted the preferred conformation to be (3) with a pyramidal nitrogen atom but with α = 20°. With other bond lengths and angles taken from the UMNDO calculations the calculated potential function for rotation about the C–N bond was found to be of the two-fold type, quite close to that of equation (2). The two minima were of equal depth, but the two maxima were slightly different in height, *i.e.* 62 and 67 kJ mol^{-1} above the minima.

The INDO-calculated h.f.s. of the amino hydrogens varied from *ca.* 4.5 to −0.3 mT, with variation of the dihedral angle θ about the C–N bond. Thus the constant A of equation (3) is predicted to be *ca.* −0.3 mT, in good agreement with the experimental result. Clearly, however, INDO predicts B values much lower than those derived from the application of equation (3). The INDO-calculated nitrogen h.f.s. varied from −0.47 to 0.97 mT with variation in θ but, as expected, the calculated h.f.s. of the propynyl hydrogens of (2a) showed relatively minor changes. The INDO h.f.s. were very sensitive to the degree of pyramidality (*i.e.* to the angle α) at nitrogen. The experimental h.f.s. are average values that vary with temperature as the populations of the torsional energy levels change, and the average value of θ changes. An estimate of the average h.f.s. $\langle a\rangle$ and their temperature variation may be obtained from the INDO-calculated h.f.s. a_θ at various values of θ and the corresponding energies E_θ (measured from the minimum in the rotational energy function) by use of the Boltzmann averaging equation (5). At low temperatures the

$$\langle a\rangle = \sum_{\theta} a_\theta \exp(-E_\theta/kT)/\sum_{\theta} \exp(-E_\theta/kT) \qquad (5)$$

amino hydrogens are confined to different potential wells and the summation is taken from $\theta = 0$ to 180° to produce two different average h.f.s. at a given temperature. At higher temperatures full rotation occurs and the summation is taken from 0 to 360°.

For the minimum-energy structure with $\alpha = 20°$ the h.f.s. calculated in this way are much greater than the experimental ones. However, reasonable agreement for the amino hydrogens and the nitrogen h.f.s. can be obtained if $\alpha = 12°$ is used and the calculated temperature dependence is shown in Figure 4. The signs of the amino h.f.s. and their change from negative to positive with increase in temperature are well reproduced. Similarly, the INDO results explain the absence of any variation in the nitrogen h.f.s. with temperature; the potential well is so deep that in the accessible temperature range the most populated torsional levels remain those with θ close to zero. The INDO-calculated h.f.s. of the amino hydrogens do not increase so steeply with temperature as the experimental h.f.s. (see Figure 4). Two factors contribute to this. Firstly, the curvature of the INDO rotational potential function does not reproduce the curvature of the true potential function. Secondly, the calculated h.f.s. do not change sufficiently greatly with variation in θ. This latter point gives an indication that the true B values are greater than those calculated by the INDO technique. The INDO calculations should not be taken as discrediting the high B values obtained from the use of equation (3).

Experimental

E.s.r. spectra were recorded with a Bruker ER 200D spectrometer on degassed samples, sealed in Spectrosil tubes, photolysed with light from a 500 W high-pressure Hg arc. Samples were examined in cyclopropane, t-butylbenzene, and/or neat di-t-butyl peroxide as solvent. The aminocyanomethane was too insoluble in the above solvents and was dissolved in acetonitrile; the best spectra were obtained with a flow system.

Allylamine, N-*Methylallylamine*, NN-*Dimethylallylamine*, *Prop-2-ynylamine*, N-*Methylprop-2-ynylamine*, *and* NN-*Dimethylprop-2-ynylamine*.—All were commercial samples and were used without further purification.

N-*t-Butylallylamine*.—Allyl bromide (60.5 g, 0.5 mol) was added dropwise over 10 min to a stirred solution of t-butylamine (73 g, 0.5 mol) in anhydrous ether (400 ml). The mixture was stirred at room temperature for 3 d, and then poured into 20% sodium hydroxide solution (250 ml). The ether layer was separated off, and most of the ether was distilled off using a short Vigreux column. Methylene dichloride was added to the ether solution, which was then dried (Na_2SO_4). The dried solution was distilled through a spinning-band column and the *N*-t-butylallylamine (5.45 g), b.p. 112 °C (lit.,[42] 112 °C) was collected; δ ($CDCl_3$) 0.84 (1 H, br s, NH, disappears on treatment with D_2O), 1.13 (9 H, s, Bu^t), 3.15—3.28 (2 H, m, CH_2NHBu^t), 4.95—5.33 (2 H, m, $CH_2{=}CH$), 5.70—6.19 (1 H, m, $CH_2{=}CH$). Distillation through a spinning-band column was necessary to obtain a pure sample of the amine.

N-*t-Butylprop-2-ynylamine*.—This was prepared similarly from prop-2-ynylamine. The amine (4.8 g) was distilled using a spinning-band column and had b.p. 125 °C (Found: C, 74.6; H, 13.2; N, 12.4. $C_7H_{13}N$ requires C, 74.3; H, 13.4; N, 12.4%); δ ($CDCl_3$) 1.12 (9 H, s, Bu^t), 1.78 (1 H, br s, NH, disappears on treatment with D_2O), 2.18 (1 H, t, J 3 Hz, $HC{\equiv}CCH_2$), 3.46 (2 H, d, J 3 Hz, $HC{\equiv}CCH_2$).

Aminoacetonitrile.—Obtained from its hydrochloride.[43]

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