

## On the Stabilization Energy of the Aminopropynyl Radical

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The stabilization energy of the aminopropynyl radical,  $\text{H}_2\text{N}\dot{\text{C}}\text{H}\equiv\text{CH}$ , was measured by using an e.s.r. technique and was found to be  $107\text{ kJ mol}^{-1}$ .

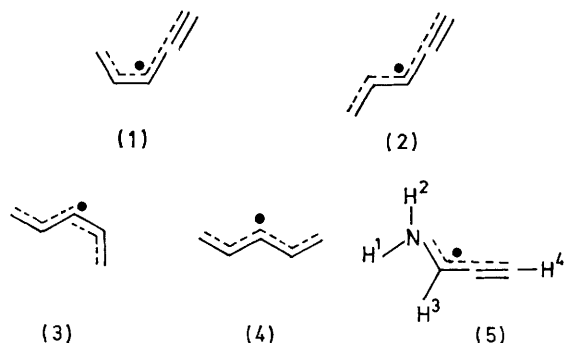
The stabilization energies,<sup>1</sup>  $E_s$ , of carbon centred radicals,  $\text{R}\cdot$ , have been the subject of extensive investigation,<sup>2,3</sup> [equations (1), (2),  $BDE =$  bond dissociation energy)]. However, the

$$BDE(\text{R-H}) = \Delta H_f(\text{R}\cdot) + \Delta H_f(\text{H}\cdot) - \Delta H_f(\text{R-H}) \quad (1)$$

$$E_s(\text{R}\cdot) = BDE(\text{CH}_3\text{-H}) - BDE(\text{R-H}) \quad (2)$$

extent to which  $E_s$  is enhanced by substitution of more than one stabilizing group at the radical centre is not well quantified. For example, in the simple series  $\cdot\text{CH}_3$ ,  $\cdot\text{CH}_2\text{CH}_3$ ,  $\cdot\text{CH}(\text{CH}_3)_2$ , and  $\cdot\text{C}(\text{CH}_3)_3$ , the additional stabilization achieved on each methyl substitution is not accurately defined because of uncertainties in the experimental values of the respective  $\Delta H_f(\text{R}\cdot)$ .<sup>3,4</sup> In the above context, the most reliable data will be available in cases where the stabilization energies are large. So far as we are aware, the only experimental data available with acceptable precision are those for allylic and propynyl substitution.

The *cis*- and *trans*-pent-1-en-4-ynyl radicals (1), (2) can be regarded as consisting of radical centres which are stabilized by an allylic and a propynyl group. E.s.r. determinations of their stabilization energies† yield  $E_s(1) = 110$  and  $E_s(2) =$



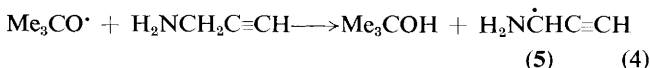
† The e.s.r. method provides data on the barrier to rotation in conjugated radicals which have been defined as their 'resonance energies'.<sup>7</sup> In this work we assume that  $E_s$  and the resonance energy are to a good approximation measures of the same molecular property.

$112\text{ kJ mol}^{-1}$ .<sup>5</sup> These values are slightly less than the sum of the stabilization energies of allyl ( $75\text{--}65\text{ kJ mol}^{-1}$ )<sup>6,7</sup> and propynyl ( $63\text{ kJ mol}^{-1}$ )<sup>8</sup> radicals. However, since the experimental error associated with each determination is *ca.*  $5\text{ kJ mol}^{-1}$  the difference may not be significant.

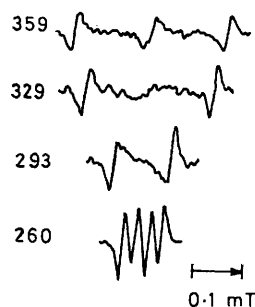
*E,Z*- and *E,E*-pentadienyl radicals, (3) and (4) can be regarded as consisting of radical centres stabilized by two allylic groups. Although the value<sup>9</sup> of  $E_s(3) = 112\text{ kJ mol}^{-1}$  is somewhat less than  $2 \times E_s(\text{allyl})$ , it should be noted that the *E,Z*-pentadienyl radical is destabilized by an internal steric interaction. While  $E_s(4)$  has not been measured, it has been shown that  $E_s(4) > E_s(3)$ . Hence, the stabilization energy of the *E,E*-pentadienyl radical may well be similar to twice that of the allyl radical.

To explore further the possibility of additivity among radical stabilization energies we have measured the  $E_s$  achieved by substitution of  $-\text{NH}_2$  and  $-\text{C}\equiv\text{CH}$  at a radical centre, *i.e.* the stabilization energy of the aminopropynyl radical (5).

The aminopropynyl radical was generated by photolysis of a solution of 3-aminopropyne in di-*t*-butyl peroxide in the cavity of an e.s.r. spectrometer, equations (3) and (4). The



spectral parameters at 370 K were  $a(\text{H}^1) = a(\text{H}^2) = 0.16$ ,  $a(\text{H}^3) = 1.47$ ,  $a(\text{H}^4) = 0.81$ , and  $a(\text{N}) = 0.52\text{ mT}$ . Those for  $\text{H}^1$ ,  $\text{H}^2$ , and  $\text{N}$  imply that there was extensive delocalization of the unpaired electron onto the nitrogen atom.<sup>10</sup> At 260 K and below,  $\text{H}^1$  and  $\text{H}^2$  had different hyperfine splittings showing that there was restricted rotation about the C-N bond. However, above this temperature rotation about the C-N bond was significant on the e.s.r. time scale as was shown by selective line broadening (see Figure 1). By 300 K,  $\text{H}^1$  and  $\text{H}^2$  were magnetically equivalent. Above the coalescence temperature relaxation matrix theory can be applied to the rate process. With the assumptions that the signal heights are inversely proportional to the squares of the total line widths and the line shapes are Lorentzian, the first-order rate constant is



**Figure 1.** Low field multiplet of the 9.4 GHz e.s.r. spectrum of the aminopropynyl radical showing the hyperfine splitting from  $H^1$  and  $H^2$  and the selective line broadening at various temperatures; *i.e.* from the top to the bottom 359, 329, 293, and 260 K, respectively.

given by equation (5),<sup>11</sup> where  $a_1$  and  $a_2$  are the hyperfine splittings (hfs) of the inequivalent  $H^1$  and  $H^2$  in the limit of

$$k/s^{-1} \rightarrow 2.5 \times 10^7 (a_1 - a_2)^2 / (\Delta H_{pp})_u [(I_u/I_b)^{\frac{1}{2}} - 1]^{-1} \quad (5)$$

slow exchange,  $(\Delta H_{pp})_u$  is the line 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. There is some uncertainty in the value of  $a_1 - a_2$  because these hfs change steeply with temperature, but at 220 K, the lowest temperature at which observations could be made,  $a_1 - a_2 = 0.05$  mT. Using this value, together with the measured unbroadened line width and the signal intensities, values of the rate constant ( $k$ ) for rotation about the C-N bond were obtained in the temperature range 300–369 K. An Arrhenius plot of the data gave  $\log(A_1/s^{-1}) = 13.7 \pm 0.7$  and  $E_a = 44 \pm 5$  kJ mol<sup>-1</sup> with a correlation coefficient of 0.985. The  $A$ -factor is normal for a process of this type which supports the use of  $a_1 - a_2 = 0.05$ ; the experimental activation energy is independent of the value taken for  $a_1 - a_2$ .

In the transition state for C-N rotation the unpaired electron is confined to the propynyl unit and the stabilization due to the amino-group is lost. Thus,  $E_s$  (5) can be regarded as being equal to  $E_s$  (propynyl)<sup>8</sup> plus the barrier for C-N bond rotation, *i.e.*  $63 + 44$  kJ mol<sup>-1</sup>. We therefore conclude that the stabilization energy of the aminopropynyl radical is 107 kJ mol<sup>-1</sup>.

The stabilization energy of the  $\alpha$ -aminomethyl radical is<sup>12</sup>  $42 \pm 8$  kJ mol<sup>-1</sup> and hence  $E_s$  (propynyl) +  $E_s$  (aminomethyl) = 105 kJ mol<sup>-1</sup>. The measured  $E_s$  (aminopropynyl) is therefore approximately equal to the sum of the stabilization energies associated with the two substituents. For pentadienyl and pentenynyl radicals the measured stabilization energies are less than the sum of the stabilization energies associated with each substituent by about 10 kJ mol<sup>-1</sup>. These differences

are, however, comparable with the experimental errors and do not rule out the possibility that  $E_s$  is an additive quantity. In theoretical calculations, Crams, Clark, and von Schleyer have pointed out that in the case of  $H_2NCHBH_2$  the stabilization energy is actually expected to be slightly greater than the sum of the contributions from the individual substituents.<sup>13</sup> When taken together the results suggest that this area of thermochemistry warrants far more detailed investigation. The general applicability of the line broadening technique employed here as a method of measuring radical stabilization energies depends on the height of the potential barrier to rotation. Barriers to internal rotation in radicals are increased above the normal single bond values by delocalisation of the unpaired electron (and other factors) which induces partial double bond character in the bond in question. The line broadening method will be applicable to radicals having suitable hfs and increased barriers in the range up to *ca.* 50 kJ mol<sup>-1</sup>.

Received, 14th June 1982; Com. 674

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