

The Role of Internal Reorganization in the Intramolecular Electron Exchange of Radical Anions of Disubstituted Benzenes

Sebastião J. Formosinho

Departamento de Química, Universidade de Coimbra, 3049 Coimbra Codex, Portugal

The alternating linewidth effects of the e.s.r. spectra of 1,3-dinitrobenzene (3-BDN) and benzene-1,3-dicarbaldehyde (3-BDC) radical anions are interpreted in terms of an intramolecular electron-exchange process with a rate constant of 10^9 s^{-1} . For 1,3-dicyanobenzene the absence of linewidth effects suggests a faster electron-exchange process ($> 10^{10} \text{ s}^{-1}$). Marcus theory and the intersecting-state model (ISM) are employed to study these electron-transfer processes. Whereas both theories predict the same rate for 3-BDN and 3-BDC, Marcus theory estimates a very low rate (*ca.* 20 s^{-1}) for dicyanobenzene radical anions whereas ISM estimates a very fast rate ($> 10^{10} \text{ s}^{-1}$) which appears to be in agreement with experiment. The reasons for the difference in the two approaches are discussed.

An essential aspect of electron-transfer reactions is the change in the equilibrium nuclear configuration of molecular species upon the gain or loss of an electron.¹ This change in configuration can involve changes in chemical bonds as well as in the orientation of the surrounding solvent molecules. Extensive theoretical studies have been carried out for solvated metal ions and metal complexes,² in contrast to the rather more limited number of studies on electron-transfer reactions of organic ions.³

Freed and Fraenkel⁴ have studied the e.s.r. spectra of several dinitrobenzene radical anions. With 1,3-dinitrobenzene an alternating linewidth effect was observed and was interpreted in terms of an asymmetric solvation of the nitro groups due to an intramolecular electron exchange process. The rates range between 1.0 and $2.5 \times 10^9 \text{ s}^{-1}$. If the exchange is very rapid ($> 10^{10} \text{ s}^{-1}$) only time-averaged values of hyperfine constants are observed and this mechanism accounts for the absence of linewidth effects of 1,2- and 1,4-dinitrobenzene radical anions.⁴ Recently Shohoji *et al.*⁵ have reported the same linewidth effects for the benzene-1,3-dicarbaldehyde (3-BDC) radical anion in ethanol, propanol, and several propanol-water mixtures. The rates of intramolecular exchange are virtually independent of solvent and range between 0.5 and $1.25 \times 10^9 \text{ s}^{-1}$. For the



exo-conformer a similar alternating linewidth effect is reported.

No linewidth effects were observed with 2- and 4-BDC radical anions.⁵ Benzene-1,2-carbaldehyde is stabilized by intramolecular hydrogen bonding,^{4,6} but for the 1,4-derivative this may be attributed to the lack of asymmetry of the mesomeric states (1,2 and 1,4) or to a fast electron-exchange process if the symmetry is lifted by hydrogen bonding with the solvent or ion pairing. With the dicyano radical anions no linewidth effects were reported in spectra with narrow linewidths.⁷

Here we study theoretically these reactions in order to give support for the intramolecular electron-transfer mechanism suggested in the literature. The reactions of 3-BDC and 1,3-dicyanobenzene radical anions are convenient systems to study, because they involve simple internal rearrangements in bond length and force constants of the substituent groups.

Marcus Theory.—According to Marcus⁸ the internal reorganizational energy for the electron exchange of 3-BDC radical anion can be estimated by writing the potential energy for the

two bonds which suffer large changes in bond lengths and force constants. Under the harmonic oscillator approximation the potential energy for the reactants, V^r , is given by equation (1) where f_i are the force constants and l_i the equilibrium bond lengths. We have assumed a symmetrical transition state of CO bond length l^* . The same expression is valid for the products. The transition state can be found by minimizing V^r in equation (1), *i.e.* $dV^r/dl^* = 0$. This condition leads to equation (2) which once substituted into (1) allows the estimation of the internal energy barrier ΔG_{in}^* .

$$2V^r = f_{C=O}(l^* - l_{C=O})^2 + f_{C-O}(l^* - l_{C-O})^2 \quad (1)$$

$$l^* = (f_{C-O}l_{C=O} + f_{C=O}l_{C-O}) / (f_{C=O} + f_{C-O}) \quad (2)$$

To estimate the internal energy barrier for electron self-exchange in 3-BDC, one has to employ force constant and bond length data typical of double and single CO bonds, because the relevant data for this radical are not known. The force constants and bond lengths are: $f_{C=O} 7.27 \times 10^3$, $f_{C-O} 3.0 \times 10^3 \text{ kJ mol}^{-1} \text{ \AA}^{-2}$, $l_{C=O} 1.215$, and $l_{C-O} 1.36 \text{ \AA}$.⁹ Equation (2) leads to $l^* 1.257 \text{ \AA}$ and through equation (1) the internal energy barrier is calculated to be $\Delta G_{in}^* 22.3 \text{ kJ mol}^{-1}$.

We have neglected any change in bond lengths and force constants of the CC bonds, because at the Lewis structure level (the level employed in the calculations for the CO bonds) they are negligible.

According to the theory of Marcus,^{2,8} the overall energy barrier for electron transfer includes also an outer-shell contribution, due to the bulk solvent reorganization. For self-exchange reactions when the spherical molecular species touch, this is given by equation (3) where γ is the solvent polarity parameter [$\gamma = (n^2 - \epsilon^{-1})$, with n the refractive index and ϵ the dielectric constant of the solvent], and r the distance between the centres of the two solvated reactant species. This expression has been criticized,¹⁰ because results for ferrocenium-ferrocene self-exchange reveal that the rates in a variety of solvents, from methanol to dimethyl sulphoxide, vary only by a factor of 2 whereas equation (3) predicts a *ca.* 20-fold variation. Self-exchange electron-transfer rates of hydrazine and hydrazine radical cation also have solvent effects an order of magnitude smaller than predicted by Marcus theory.¹¹

$$\Delta G_{out}^* / \text{kJ mol}^{-1} = 347\gamma / 2(r/\text{\AA}) \quad (3)$$

Possibly the most surprising results are the recent findings of Nelsen *et al.*¹² Electron transfer of several alkylhydrazines^{0/+} in solution and in the vapour phase has similar energy barriers; in

one case ΔG^* is even higher in the vapour phase. Although these results reveal the importance of the changes in geometry for these electron-transfer processes, they reveal also that the outer-shell reorganization is negligible. For example, the estimation of ΔG_{out}^* in acetonitrile (γ 0.527) for these systems, according to Marcus theory, leads to $\Delta G_{\text{out}}^* \approx 9 \text{ kJ mol}^{-1}$, which implies electron-transfer rates *ca.* 2×10^{-2} times slower in solution, contrary to the experimental findings.

This situation apparently requires a modification in the estimation of the outer-shell contribution for the electron-transfer reactions. Sacher and Laidler¹³ estimate the solvent reorganization in terms of the reorientation of solvent dipoles around an electrical charge. For the reaction $A^{z+/(z-1)^+}$ equation (4) holds where n_D is the number of the solvent dipoles which surround the ions, μ is the dipole moment, r' is the distance between the centre of charge and the solvent molecules, and r^* is the same distance for the transition state. For a single dipole associated with the CO bonds through hydrogen bonding, r' can be estimated as half the CO bond length plus the radius of a water molecule ($2r' = l_{\text{CO}} + 2.76 \text{ \AA}$). The change in r^* at the transition state can be estimated through equation (2) and leads to a negligible solvent reorganization ($< 2 \text{ kJ mol}^{-1}$).

$$-\Delta G_{\text{out}}^* = n_D \mu \epsilon \{ [(2Z - 1)/r^{*2}] - [Z/r'_{\text{ox}}{}^2] - [(Z - 1)/r'_{\text{red}}{}^2] \} \quad (4)$$

Such an estimation of ΔG_{out}^* associated with the previously calculated internal energy barrier gives an overall energy barrier of $\Delta G^* \approx 22 \text{ kJ mol}^{-1}$ in good agreement with experiment. For an adiabatic electron-transfer reaction, within Transition State Theory,^{*} with equation (5), the estimated rate constant at room temperature is $0.9 \times 10^9 \text{ s}^{-1}$, which is in good agreement with the experimental values of $0.5 - 1.25 \times 10^9 \text{ s}^{-1}$, virtually solvent independent (hydrogen bonding).⁵

A similar calculation can be carried out for the electron-exchange process in the radical anion of 1,3-dicyanobenzene.⁷ With $f_{\text{C=N}} 1.1 \times 10^4$, $f_{\text{C=N}} 6.3 \times 10^3 \text{ kJ mol}^{-1} \text{ \AA}^{-1}$, $l_{\text{C=N}} 1.157$, and $l_{\text{C=N}} 1.34 \text{ \AA}$,⁹ equation (2) leads to $l^* 1.225 \text{ \AA}$ and equation (1) gives $\Delta G_{\text{in}}^* 66 \text{ kJ mol}^{-1}$. Again one can neglect the external solvent reorganization. Thus, Marcus theory provides a very low estimation for the electron-transfer rate constant ($k 20 \text{ s}^{-1}$).[†] With such a rate, pronounced linewidth effects should have been observed in e.s.r. spectra contrary to experimental observations,⁷ which suggests a rate constant $> 10^{10} \text{ s}^{-1}$. Such a high rate is not surprising, because the electron-exchange reaction between the benzonitrile negative anions and the parent compound is already very fast, $k > 2 \times 10^8 \text{ s}^{-1}$.¹⁴

$$k = (k_B T/h) \exp [-(\Delta G^*/RT)] \quad (5)$$

For electron-transfer reactions between metal ions such discrepancies between theory and experiment are currently interpreted in terms of alternative mechanisms for the reactions, such as, for example, with the $\text{Co}_{(\text{aq})}^{2+/3+}$ system.¹⁵ However, for the radical anions under consideration this does not seem to be a feasible explanation. Nuclear tunnelling is thought to be important only at the onset of the inverted region, but in any case does not account for discrepancies of nine orders of magnitude.

* The experimental data were analysed by Transition State Theory, with a pre-exponential factor of $1.3 \times 10^{13} \text{ s}^{-1}$ and $E_a 22.3 \text{ kJ mol}^{-1}$ for 3-BDC.⁵

† Within the present level of approximation we have employed the limiting distances of C-O, C=O, also C=N and C≡N, to calculate Δl . Therefore, the Δl values can be smaller, but, in relative terms, the discrepancy between the calculations for 3-BDC and 1,3-dicyanobenzenes remains.

Tunnelling of an electron may be also considered, because the dicyanobenzene radical anion has a lower ionization potential, I , than the carbaldehydes. For a rectangular barrier of height I ^{16,17} equation (6) holds where ν is the frequency of the electronic movement in molecules ($\nu 10^{15} - 10^{16} \text{ s}^{-1}$), m is the mass of the electron, and Δx is the width of the barrier; Δx is taken as the distance between the nitrogen atoms ($\Delta x 7.3 \text{ \AA}$), where the negative charges are mainly localized. The ionization energy of 1,3-dicyanobenzene in solution is not known, but a rough estimation of I of *ca.* 5 eV can be made from a correlation of ionization energies¹⁸ of atoms and benzene derivatives and the ionization energies of the corresponding anions in solution;¹⁹ the estimation gives $I 5.5 \text{ eV}$ for $\text{C}_6\text{H}_5\text{CN}^-$ and a slightly smaller value is employed for the disubstituted compound. With this set of parameters the estimated rate of electron tunnelling ranges between 5×10^7 and $5 \times 10^8 \text{ s}^{-1}$, too low to account for the e.s.r. rate of electron transfer.

$$k_{\text{tun}} = \nu \exp [-(4\pi/h)(2mI)^{1/2} \Delta x] \quad (6)$$

The Intersecting-state Model.—It appears that the theory of Marcus overestimates considerably the energy barrier of electron-transfer exchange in 1,3-dicyanobenzene radical anion. In order to investigate this problem further, it is useful to consider two limiting situations which do not obey Badger's rule:²⁰ (i) $f_{\text{ox}} = f_{\text{red}}$ and $l_{\text{ox}} \neq l_{\text{red}}$ and (ii) $f_{\text{ox}} \neq f_{\text{red}}$ and $l_{\text{ox}} = l_{\text{red}}$.[‡] For both these limiting situations one expects that there will be an internal energy barrier, because there are changes in the potential energy from the oxidized to the reduced species. However, equations (1) and (2) reveal that for situation (ii) Marcus theory leads to $\Delta G_{\text{in}}^* 0$. The problem arises because this theory, which follows the Principle of Least Motion,²² leads to a transition state bond length that is intermediate between those of oxidized and reduced species, $l_{\text{ox}} \leq l^* \leq l_{\text{red}}$.

One way to circumvent this problem is to minimize the potential energy along the reaction co-ordinate, with the assumption that $l^* > l_{\text{ox}}, l_{\text{red}}$, *i.e.*, the reactive bonds of the oxidized and reduced species expand in an 'explosion' at the transition state. As shown in the Appendix this assumption can be justified within a LEPS potential function.

An adequate model to estimate barrier heights for such a path is the recently developed intersecting-state model (ISM).²³ For a thermoneutral electron-transfer process, which involves the change in length of chemical bonds of stretching force constants f of reactant and product, then equation (7) applies where x is the bond extension of the reactant and d is the sum of the bond extensions of reactant and product, $d = (l^* - l_r) + (l^* - l_p)$. Within ISM d , which also represents the horizontal displacement of the potential energy curves of reactant and product, is > 0 .

$$(1/2)f_r x^2 = (1/2)f_p (d - x)^2 \quad (7)$$

$$\Delta G^* = (1/2)f_r x^2 \quad (8)$$

The energy barrier is equation (8) where x is estimated through equation (7), once d is known. We have shown²³ that for a thermoneutral reaction, equation (9) applies where n^* is the bond order of the transition state and a' is a constant. Within ISM the interaction between the electronic states which leads to a resonance splitting, ϵ , of the potential energy curves at the crossing point is included in the parameter d . For a vast number of chemical reactions ϵ appears to be universal and leads to a value of 0.156 for the constant a' .

‡ $\text{Fe}(\text{phenanthroline})_3^{2+/3+}$ appears to be an example of this case, because the iron-nitrogen bonds in these complexes have virtually the same length, $l_{\text{ox}} 1.973$ and $l_{\text{red}} 1.97 \text{ \AA}$.²¹

$$d = (a' \ln 2/n^*)(l_r + l_p) \quad (9)$$

Let us consider first the 3-BDC radical anion which involves bond extensions of the C=O and C-O bonds. One can consider $f_r = f_p = (f_{C=O} + f_{C-O})/2$, and the transition state bond order as the average of a double and a single bond, *i.e.*, $n^* 1.5$. With the previously reported force constants and bond lengths one can estimate the barrier height through equations (7)–(9). The estimated value is $\Delta G_{in}^* 22 \text{ kJ mol}^{-1}$. For the estimated sum of bond extensions, $d 0.185 \text{ \AA}$, the external solvent reorganization calculated through equation (4) is negligible ($< 1 \text{ kJ mol}^{-1}$). So the estimated energy barrier provides also a calculated rate ($9 \times 10^8 \text{ s}^{-1}$) at room temperature in good agreement with experiment.⁵

A demanding test of ISM is the calculation of electron exchange for the radical anion of 1,3-dicyanobenzene. With the set of data previously reported and an average bond order between a triple and a double bond, $n^* 2.5$, the estimated barrier height is $\Delta G^* 12.5 \text{ kJ mol}^{-1}$ which corresponds to a rate constant of $4.5 \times 10^{10} \text{ s}^{-1}$ in agreement with experimental observations.⁴

In contrast with Marcus theory, the intersecting-state model seems adequate to deal with electron exchanges in radical anions of benzene derivatives. It appears that in an electron-transfer reaction there are internal modes, which may be called 'passive modes', where l^* is intermediate between the equilibrium bond lengths of reactant and product and others, 'active modes', which suffer an expansion at the transition state. One expects that, in general, the 'passive modes' will be the ones which suffer a small change in bond lengths and/or force constants between reactants and products.* Consequently, their contribution for ΔG_{in}^* is small, but should be added to the more significant contribution of the 'active modes'. In the present study we have neglected the contribution of the CC 'passive modes', because we have considered that for them f and l do not change between reactant and product.

It may be argued that in the case of mesomeric states there is no activated electron transfer as in the case of the *meta*-compounds. However, this result is model dependent. For example, theoretical calculations in the benzenedicarbaldehydes show that the mesomeric effects are negligible and the π_{C-CO} Mulliken overlap populations in benzaldehyde and the *o*-, *m*-, and *p*-benzenedicarbaldehydes are nearly equal and, consequently, intramolecular electron exchange appears to be feasible in benzene-1,4-dicarbaldehyde.²⁵ In solution such asymmetry may be stabilized through interactions with solvent molecules or cations present in the system. Nevertheless, the e.s.r. spectrum of 4-BDC shows no line-width effects.^{4,5} If this fact is attributed to a fast electron exchange ($k > 10^{10} \text{ s}^{-1}$), one can recognize that the *para* (*ortho*) position of the substituent groups of these derivatives allows electronic coupling with the aromatic ring. Such coupling leads to an electronic siphoning into the transition state which increases n^* .²⁶ For a completely delocalized system the increase in n^* can amount to 0.5 corresponding to the siphoning of a pair of electrons for two bonds, C=O and C-O. With $n^* 2$ the calculated energy barrier decreases from $\Delta G^* 22$ to 11 kJ mol^{-1} , which corresponds to a rate of $8 \times 10^{10} \text{ s}^{-1}$. So the observed rate of electron exchange should be $9 \times 10^8 \text{ s}^{-1} < k \leq 8 \times 10^{10} \text{ s}^{-1}$, too high to lead to any observable linewidth effects in e.s.r. spectra.

A final word should be said about the effects of solvent on ΔG_{in}^* and on the stability of ISM to small errors. The good agreement with experiment using $f_{C=O}$ and $l_{C=O}$ for the CO^-

bond may appear surprising. This is an approximation in view of the lack of experimental data for such bond. If *e.g.* one assumes that instead of $n = 1$, the CO^- has a bond order, $n = 0.9$, according to the Pauling relation²⁷ between bond orders and lengths, and Badger's rule,²⁰ $f_{CO^-} 2.66 \times 10^3 \text{ kJ mol}^{-1} \text{ \AA}^{-2}$ and $l_{CO^-} 1.388 \text{ \AA}$. With $n^* 1.455$ this set of data leads to $\Delta G_{in}^* 23 \text{ kJ mol}^{-1}$. For $n 1.1$ then $f_{CO^-} 3.4 \times 10^3 \text{ kJ mol}^{-1}$ and $l_{CO^-} 1.33 \text{ \AA}$ and with $n^* 1.55 \Delta G_{in}^*$ is 21 kJ mol^{-1} . A decrease in f is currently associated with an increase in l , and an increase in f corresponds to a decrease in l . These two effects tend to compensate for the estimation of the energy barrier.

Variations in the polarity of the solvent will lead to variations in the force constant and bond length of the CO^- bond. However, the solvent effect on ΔG_{in}^* is expected to be small owing to the compensating effect of f and l .

The similarity of the bond length data of the CO and NO single and double bonds⁹ may imply a similar behaviour of the force constants and, eventually, of the electron-transfer rates of the dinitrobenzene and benzenedicarbaldehyde radical anions ($k 1-2.5 \times 10^9 \text{ s}^{-1}$ for 1,3-dinitrobenzene radical anion and $k > 10^{10} \text{ s}^{-1}$ for the 1,2 and 1,4 derivatives⁴). However, it should be pointed out that for NO_2 and NO_2^- one has to define an effective force constant along the reaction co-ordinate, which depends on the force constant of each NO bond. Furthermore, solvents can alter not only f and l for such bonds, but also the bending force constant and the equilibrium position of the \widehat{ONO} angle. The bending mode, which can be treated as a 'passive mode', has no compensation of effects on ΔG_{in}^* . Therefore solvent effects are expected to be more significant for the nitro-derivatives than for 3-BDC, which may explain the stronger variation on the rates of exchange for 1,3-dinitrobenzene radical anions from water (slower) to dimethylformamide (faster).

Appendix

Transition State Bond Lengths for a LEPS Potential Function.—For an electron-transfer reaction $A^+ + BC \longrightarrow A + BC^+$ let us assume a hypothetical situation where the equilibrium bond lengths (R_e) of BC and BC^+ are identical. For a LEPS (London-Eyring-Polanyi-Sato) potential function,²⁸ it has been shown²⁹ that for a symmetrical collinear stationary

$$\frac{1}{2} \left[3 \left(\frac{dV(S)}{dR} \right)_0 + \left(\frac{dV(T)}{dR} \right)_0 \right] + 2 \left(\frac{dV(T)}{dR} \right)_{00} = 0 \quad (A-1)$$

point, equation (A-1) holds where $V(S)$ and $V(T)$ represent the diatomic potentials for the singlet and triplet respectively, and R is the internuclear separation. The subscripts 0 and 00 indicate the value of R at which the potential function or its derivative must be evaluated $R = R_{sp}$ (saddle point) and $R = 2R_{sp}$.

We demonstrate that $R_{sp} > R_e$. If $R_{sp} = R_e$ then $(dV(S)/dR)R_e = 0$ and from equation (A-1), we have (A-2) which is not

$$\frac{1}{2} \left(\frac{dV(T)}{dR} \right)_e = -2 \left(\frac{dV(T)}{dR} \right)_{ee} \quad (A-2)$$

valid for the repulsive potential energy curve, owing to the change of sign of the derivative.

If $R_{sp} < R_e$ then $(dV(S)/dR)_0 < 0$ and from equation (A-1) we have (A-3). This implies the existence of a minimum in the

$$\frac{1}{2} \left(\frac{dV(T)}{dR} \right)_0 + 2 \left(\frac{dV(T)}{dR} \right)_{00} > 0 \quad (A-3)$$

triplet potential energy curve between R_{sp} and R_{2sp} , which is at variance with the repulsive character of the triplet curve. Consequently, $R_{sp} > R_e$.

* This is not a universal rule. See, for example, the role of the C≡N bond as an 'active mode' in the proton-transfer reactions of HCN which, when included in the reaction co-ordinate, provides a lower energy barrier due to an increase in n^* .²⁴

Acknowledgements

I am grateful to Professor B. J. Herold for calling my attention to this problem and for many fruitful discussions, to Professor A. J. C. Varandas for his suggestion on the use of the LEPS potential functions, and to the referees for useful comments.

References

- 1 W. F. Libby, *J. Phys. Chem.*, 1952, **56**, 73.
- 2 For a recent review see R. A. Marcus and N. Sutin, *Biochim. Biophys. Acta*, 1985, **811**, 265.
- 3 See for example J. Eriksen, K. A. Jorgensen, J. Linderberg, and H. Lund, *J. Am. Chem. Soc.*, 1984, **106**, 5083; G. Grampp, *Z. Phys. Chem. Neue Folge*, 1986, **148**, 53.
- 4 J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, 1962, **37**, 1156; 1964, **41**, 699.
- 5 M. C. B. L. Shohoji, B. J. Herold, H. M. Novais, and S. Steenken, *J. Chem. Soc., Perkin Trans. 2*, 1986, 1465.
- 6 B. J. Herold, M. das Mercês, V. Marques, H. M. Novais, S. Steenken, and H. Hermann, *Radicaux Libres Organiques, Coll. Int. CNRS*, 1978, **278**, 73.
- 7 P. H. Rieger, I. Bernal, W. H. Reinmuth, and G. K. Fraenkel, *J. Am. Chem. Soc.*, 1963, **85**, 683.
- 8 R. A. Marcus, *J. Chem. Phys.*, 1965, **43**, 679.
- 9 A. J. Gordon and R. A. Ford, 'The Chemist's Companion,' Wiley, New York, 1972, pp. 107 and 114.
- 10 T. Gennett, D. F. Milner, and M. J. Weaver, *J. Phys. Chem.*, 1985, **89**, 2787.
- 11 S. F. Nelsen and S. C. Blackstock, *J. Am. Chem. Soc.*, 1985, **107**, 7189.
- 12 S. F. Nelsen, D. T. Rumock, and M. Meot-Ner (Mautner), *J. Am. Chem. Soc.*, 1987, **109**, 1373.
- 13 E. Sacher and K. J. Laidler, *Trans. Faraday Soc.*, 1963, **59**, 396.
- 14 P. Ludwig and R. N. Adams, *J. Chem. Phys.*, 1962, **37**, 828.
- 15 J. F. Endicott, B. Durham, and K. Kumar, *Inorg. Chem.*, 1982, **21**, 2437.
- 16 See for example, R. P. Bell, 'The Tunnel Effect in Chemistry,' Chapman and Hall, London, 1980, p. 21.
- 17 I. V. Alexandrov, R. F. Khairutdinov, and K. I. Zamaraev, *Chem. Phys.*, 1978, **32**, 123.
- 18 'Handbook of Chemistry and Physics,' Chemical Rubber Co., Cleveland, 53 edn., 1972, p. E-62.
- 19 R. G. Pearson, *J. Am. Chem. Soc.*, 1986, **108**, 6109.
- 20 R. M. Badger, *J. Chem. Phys.*, 1934, **2**, 128; 1935, **3**, 710.
- 21 B. S. Brunshwig, C. Creutz, D. H. McCartney, T. K. Sham, and N. Sutin, *Faraday Discuss. Chem. Soc.*, 1982, **74**, 113.
- 22 F. O. Rice and E. Teller, *J. Chem. Phys.*, 1938, **6**, 489; 1939, **7**, 199.
- 23 A. J. C. Varandas and S. J. Formosinho, *J. Chem. Soc., Faraday Trans. 2*, 1986, **82**, 953.
- 24 S. J. Formosinho and V. M. S. Gil, *J. Chem. Soc., Perkin Trans. 2*, 1987, 1655.
- 25 H. Lumbroso, C. Liègeois, G. C. Pappalardo, and V. Librando, *J. Mol. Struct.*, 1980, **62**, 195.
- 26 S. J. Formosinho, *Tetrahedron*, 1986, **42**, 4557.
- 27 L. Pauling, *J. Am. Chem. Soc.*, 1947, **69**, 542.
- 28 S. Sato, *J. Chem. Phys.*, 1955, **23**, 592, 2465.
- 29 A. J. C. Varandas, *J. Chem. Phys.*, 1979, **70**, 3786.

Received 7th January 1987; Paper 7/029