bands, with slight relative intensity differences, as the 457.9-nm spectrum.[11]

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(12) E. Konig and E. Lindner, *Spectrochim. Acta, Part A*, **28**, 1393 (1972).

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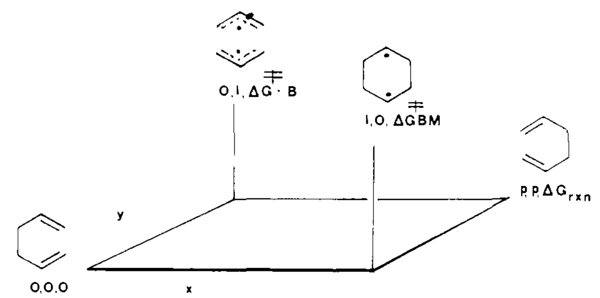
Substituent Effects in Concerted Reactions. A Nonlinear Free-Energy Relationship for the 3,3-Shift and the Diels-Alder Reaction

Sir:

Prediction of absolute rate constants for and substituent effects on concerted pericyclic reactions is useful in synthesis. However, a Hammett LFER approach is inappropriate since transition-state structure can change dramatically with substituents. For instance, the transition-state structure in 3,3 shifts of variously substituted 1,5-hexadienes as deduced from secondary deuterium isotope effects varies substantially between the nonconcerted alternatives resulting from either C_3C_4 bond breaking or C_1C_6 bond making.[1] This relationship can be quantified using the simplest equation for a three-dimensional energy surface with a saddle point, namely, $\Delta G = ax + by + cxy + d$,[2] and the proper boundary conditions. If the reactant is at $x = 0$, $y = 0$, then $\Delta G = 0$ and $d = 0$. If, at $x = 1$, $y = 0$, the pure bond-making transition state is achieved, then $a = \Delta G^{\ddagger}(\mathrm{BM})$. If, at $x = 0$, $y = 1$, the pure bond-breaking transition state is achieved, then $b = \Delta G^{\ddagger}(\mathrm{BB})$. If the product is at an average position $x = p$, $y = p$, then $c = [(\Delta G_{\mathrm{rxn}}/p) - \Delta G^{\ddagger}(\mathrm{BB}) - \Delta G^{\ddagger}(\mathrm{BM})]/p$. Setting the partial derivatives of ΔG with respect to x and to y equal to zero allows determination of the transition-state position which upon substitution in the original equation gives

$$\Delta G^{\ddagger} = [\Delta G^{\ddagger}(\mathrm{BB})*\Delta G^{\ddagger}(\mathrm{BM})*p]/[\Delta G^{\ddagger}(\mathrm{BB}) + \Delta G^{\ddagger}(\mathrm{BM}) - (\Delta G_{\mathrm{rxn}}/p)] \quad (1)$$

Scheme I



where p is an empirically determined parameter. Remarkably, for all of the 3,3 shifts, p is a constant and equal to 1.5. The calculated and experimental $\Delta G^{\ddagger}$ values are shown in Table I. The significance of p in eq 1 is that it adjusts the magnitude of $\Delta G^{\ddagger}$ and therefore represents the extent of coupling of the nonconcerted alternatives; it is the non-LFER equivalent of the Hammett ρ.

Highly notable exceptions to the simple formula are the 3,3 shift of *cis*-1,2-divinylcyclopropane[3] and of allyl silyl enol esters[4] (see Table I). A reasonable rationalization for the first is the possible strong coupling of the vinyl groups and the π-like electrons of cyclopropane ring in the ground state. The second may be due to inordinant stabilization of the bond-making alternative by, if not actual rearrangement of, the Me_3Si group. Thus, exceptions to the simple formula may indicate reactions requiring special scrutiny.

While derived from a crude model, eq 1 makes chemically reasonable predictions about the response of $\Delta G^{\ddagger}$ to substituent changes that affect ΔG_{rxn}, $\Delta G^{\ddagger}(\mathrm{BM})$, and $\Delta G^{\ddagger}(\mathrm{BB})$. However, careful scrutiny of eq 1 reveals that it can be applied to neutral or exergonic reactions but not to highly endergonic ones unless certain terms are redefined.[5]

Table I. ΔG Values at 523 K for Various 3,3 Shifts

compd	$\Delta G^{\ddagger}_{\mathrm{xp}}$	$\Delta G^{\ddagger}_{\mathrm{calcd}}$[a]	$\Delta G^{\ddagger}(\mathrm{BB})$	$\Delta G^{\ddagger}(\mathrm{BM})$[c,d]	ΔG
1,5-hexadiene	41[e]	41.2	57[b]	53	0
2-phenyl-	35.5[f]	36.3	57	42	0
2,5-diphenyl-	31[f]	30.1	57	31	0
3,3-dicyano-	32[g]	31.6	37	53	~−4.5
threo-3,4-dimethyl-	39[h]	38.7	53	53	−4.5
threo-3,4-diphenyl-	31[i]	30.6	35	53	~−4.5
cis-1,2-divinylcyclobutane	28[j]	28.6	34[k]	60[l]	−19
allyl vinyl ether	33[m]	33.6	47[n]	53[n]	−17
allyl phenyl ether	42[o]	43.2	47[p]	69[n]	+5[h]
allyl acetate	45[f]	43.9	52[n]	67[n]	0
cis-1,2-divinylcyclopropane	21[r]	27.5	35[s]	53	−20
allyl silyl enol acetate	<25[t]	33	47	53	−20
3-oxy anion 1,5-hexadiene	~26[u]	23.4[v]	26[w]	53	−19[v]

[a] Calculated according to eq 1 with $p = 1.5$. [b] D. M. Golden, N. A. Gac, and S. W. Benson, *J. Am. Chem. Soc.*, **91**, 2136 (1969). [c] See ref 1. [d] Some of the values are calculated using the resonance energies of benzyl radical = 11 kcal/mol, α-CN radical = 9 kcal/mol, and α-Me radicals = 2 kcal/mol. [e] W. von E. Doering, V. G. Toscano, and G. H. Beasley, *Tetrahedron*, **27**, 5299 (1971). [f] M. J. S. Dewar and L. E. Wade, *J. Am. Chem. Soc.*, **99**, 4417 (1977). [g] F. G. Foster, A. C. Cope, and F. Daniels, *ibid.*, **69**, 1893 (1947). [h] W. von E. Doering and W. R. Roth, *Tetrahedron*, **18**, 67 (1962) and ref 1. [i] R. P. Lutz and H. A. J. Berg, private communication, 1978. [j] W. von E. Doering, M. Frank-Newman, D. Hasselmann, and R. L. Kaye, *J. Am. Chem. Soc.*, **94**, 3833 (1972). [k] Free energy for cleavage and isomerization of *trans*-1,2-divinylcyclobutane minus 1 kcal/mol for the strain of a *cis*-1,2-divinyl relationship; see *j*. [l] For a boat diyl, −7 kcal/mol destabilization over chair is assumed. [m] F. W. Schuler and G. W. Murphy, *J. Am. Chem. Soc.*, **72**, 3155 (1950). [n] Calculated according to S. W. Benson, "Thermochemical Kinetics", 2nd ed., Wiley, New York, 1976; these values are at 298 K. [o] For a review, see S. J. Rhoads and R. N. Rawlins, *Org. React.*, **22**, 1 (1975). [p] K. W. Egger and A. T. Cocks, *Helv. Chim. Acta*, **56**, 1517 (1973). [q] E. S. Lewis, J. T. Hill, and E. R. Newman, *J. Am. Chem. Soc.*, **90**, 662 (1968). [r] Reference 3. [s] E. Vogel, *Angew. Chem.*, **72**, 4 (1960); E. Vogel et al., *Justus Liebigs Ann. Chem.*, **644**, 172 (1961); R. Sunderman, Ph.D. Dissertation, Köln, 1966, as quoted by M. R. Willcott, R. L. Cargill, and A. B. Sears, *Prog. Phys. Org. Chem.*, **9**, 50 (1972). [t] Reference 4. [u] Potassium salt in THF and 18-crown-6: D. A. Evans and A. Golob, *J. Am. Chem. Soc.*, **97**, 4765 (1975). [v] In the gas phase. [w] ΔG to acrolein and allyl anion, in gas phase at 25 C, not ΔG to acrolein radical anion and allyl radical which is ~15 kcal/mol higher; see M. L. Steigerwald, W. A. Goddard III, and D. A. Evans, *ibid.*, **101**, 1994 (1979).

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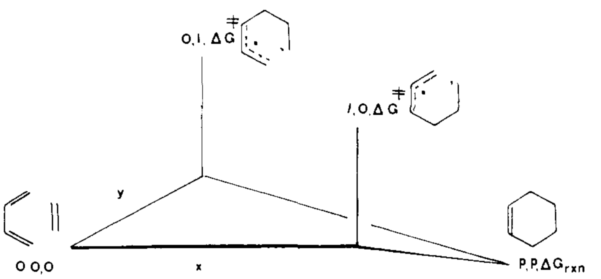
Table II. Experimental and Calculated $\Delta G^{\ddagger}$ Values and Relative Rate Constants for Cycloaddition of Dienophiles with Cyclopentadiene at 293 K

dienophile	$\Delta G^{\ddagger}{}_{\mathrm{xp}}{}^{a}$	$\Delta G^{\ddagger}{}_{\mathrm{calcd}}{}^{b}$	$k_{\mathrm{rel}}{}^{\mathrm{xp}}$	$k_{\mathrm{rel}}{}^{\mathrm{calcd}}$
ethylene		27.67	2.5×10^{-5} (estd)[9]	1.48×10^{-3}
acrylonitrile	24.07	23.76	1	1
fumaronitrile	21.27		78	
		20.63		184
maleonitrile	21.06		88	
1,1-dicyanoethylene	17.84	18.89	43×10^{3}	4.2×10^{3}
1,1,2-tricyanoethylene	16.37	16.6	$\sim 46 \times 10^{4}$	15×10^{4}
1,1,2,2-tetracyanoethylene	13.85	13.7	$\sim 41.4 \times 10^{6}$	19×10^{6}

[a] A. Sauer, H. Wiest, and A. Mielert, *Ber.*, **97,** 3183 (1964). [b] Calculated according to eq 1 with $\Delta G^{\ddagger}(\mathrm{BR}_1) = \Delta G^{\ddagger}(\mathrm{BR}_2) = 40$ kcal/mol for ethylene, $p = 1.6$, $\Delta G_{\mathrm{rxn}} = -20$ kcal/mol and α-CN radical resonance energy = 9 kcal/m.

It is useful to examine the response of the Diels–Alder reaction of cyano-substituted dienophiles with cyclopentadiene. The appropriate nonconcerted derivatives are shown in Scheme II. While none of the thermochemical quantities have been determined experimentally, it is possible to estimate them using Benson's group additivity relations.[6] However, since only relative $\Delta G^{\ddagger}$ values shall be calculated, these values need not be estimated with more than moderate accuracy. What is important is that activation free energies of the nonconcerted alternatives will decrease by the value of the α-cyano radical resonance energy (9 kcal/mol).[7] With $p = 1.6$ the values of $\Delta G^{\ddagger}$ for all of the various cyanosubstituted dienophiles can be reproduced within 1.0 kcal/mol and the relative rates calculated to not differ by more than a factor of 2 to 10 from those observed (see Table II).

Scheme II



This model of substituent effects does not prove that the Diels–Alder reaction is concerted; other experimental work is far more persuasive in this regard,[8] but it does nicely rationalize substituent effects cited as evidence against concert.[9] However, other substituents and dienes must be pursued within this framework before general applicability can be claimed. In particular, steric effects may also play an important role, and these are currently being analyzed.[10-13]

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References and Notes

(1) See J. J. Gajewski and N. D. Conrad, *J. Am. Chem. Soc.*, **100,** 6268, 6269 (1978), and references cited therein.

(2) For this and other examples, see S. I. Miller, *J. Am. Chem. Soc.*, **81,** 101 (1959); J. E. Critchlow, *J. Chem. Soc., Faraday Trans. 1*, **68,** 1774 (1972); D. A. Jencks and W. P. Jencks, *J. Am. Chem. Soc.*, **99,** 7948 (1977), and references cited therein. See also note 11 of this paper.

(3) J. M. Brown, B. T. Golding, and J. J. Stufko, Jr., *J. Chem. Soc., Chem. Commun.*, 319 (1973).

(4) R. E. Ireland, R. H. Mueller, and A. K. Willard, *J. Am. Chem. Soc.*, **98,** 2868 (1976).

(5) J. M. Warner, unpublished work.

(6) S. W. Benson, "Thermochemical Kinetics", 2nd ed., Wiley, New York, 1976.

(7) W. von E. Doering, G. Horowitz, and K. Sachdev, *Tetrahedron*, **33,** 273 (1977).

(8) H. M. Frey and R. Pottinger, *J. Chem. Soc., Faraday Trans. 1*, 1827 (1979); see also J. A. Berson, P. B. Dervan, R. Malherbe, and J. A. Jenkins, *J. Am. Chem. Soc.*, **98,** 5937 (1976), and R. E. Townshend, G. Ramunni, G. Segal, W. J. Hehre, and L. Salem, *ibid.*, **98,** 2190 (1976).

(9) (a) M. J. S. Dewar, S. Olivella, and M. S. Rzepa, *J. Am. Chem. Soc.*, **100,** 5650 (1978). (b) J. W. McIver, *Acc. Chem. Res.*, **7,** 72 (1974); *J. Am. Chem. Soc.*, **97,** 3632 (1974).

(10) Equation 1 is being applied to ionic reactions with Professor J. E. Bartmess, paper in preparation.

(11) (a) Other models for the reaction have been examined including quantum mechanical coupling, but none has reproduced the free-energy data as well as eq 1. (b) Interestingly, Professor Bartmess, using a computer model for digital solution of Lapalce's equation,[11c] has generated a surface equivalent to that generated by $Z = ax + by + cxy$. (c) R. E. Kaufman, "A Fortran Coloring Book", the MIT Press, Cambridge, Mass., 1978, pp. 255-263.

(12) (a) Equation 1 generates a "band shell" surface and provides insight into Hammett plots. In particular, the only way a Hammett plot can have a minimum is if the two coupled alternatives are near equivalent in free energy. Thus, in the substitution of benzyl bromide by radioactive bromide,[12b] the bond-breaking extreme (benzyl cation and associated particles) and the bond-making extreme (pentavalent carbon anion) must have nearly equivalent free energies! (b) S. Sugdeon and J. B. Willis, *J. Chem. Soc.*, 1360 (1951).

(13) (a) Equation 1 and the definitions leading to it allow calculation of the transition-state position. Unfortunately, the position does not correspond to the relative KIE's observed. However, the KIE's in the 3,3 shift can be reproduced by appropriate application of Miller's equation[13b] to the parallel and perpendicular coordinates[13c] of the energy surface. (b) A. R. Miller, *J. Am. Chem. Soc.*, **100,** 1984 (1978). (c) E. R. Thornton, *ibid.*, **89,** 2915 (1969).

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Charge-Transfer Luminescence from a Nonaromatic α-Diimine Complex of Ruthenium(II)

Sir:

Since the introduction of tris(2,2′-bipyridine)ruthenium(II), $[\mathrm{Ru(bpy)_3}]^{2+}$, as a photosensitizer,[1] there has been a surge of interest in the excited-state properties and chemistry of $[\mathrm{Ru(bpy)_3}]^{2+}$ and related polypyridine complexes of d^6 metals.[2,3] This interest has been augmented in part by their potential utilization in solar energy conversion and in laser applications.[4,5]

To date all charge-transfer (CT) emissions from Ru(II) complexes have occurred with molecules containing aromatic bipyridines, phenanthrolines, and their isoelectronic nitrogen substituted ligand analogues.[5a,6-8] We report here proof that an aromatized cyclic ligand is not essential for CT emission. CT emissions can arise when only the α-diimine (-N=C—C=N-) functionality or at most a perturbed α-diimine is present. This result opens up a broad new class of ligands[9] for preparing potential CT emitting photosensitizers.

We have prepared the tris(2,2′-bi-2-thiazoline)ruthenium(II) complex,[10] $[\mathrm{Ru(bt)_3}]^{2+}$, where bt has the following structure.

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