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Intramolecular thermal ($4\sigma + 2\pi$) dyotropy: primary ^{2}H kinetic isotope effects. Experimental limiting barrier parameters for quantum tunnelling in 2H transfer processes and mechanistically significant substituent effects

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ABSTRACT: Primary deuterium kinetic isotope effects (PDKIE) in parazoline-annelated *syn*-sesquinorbornenes exhibiting irreversible intramolecular ($4\sigma + 2\pi$) thermal dyotropy reveal unambiguous evidence for a tunnelling contribution to the kinetics in one instance but not for a close analogue. For analogous dyotropy of a cyclohexadiene-annelated *syn*-sesquinorbornene, the tunnelling components of the kinetic behaviour is small by comparison. The H atom traverse between alternative loci for the pyrazolines, deduced from x-ray and neutron diffraction data, is in agreement with approximate barrier parameters obtained by fitting of the PDKIE data to the Bell equation; barrier penetration is 3.22 kcal below the computed barrier corrected for the tunnelling contribution. The relative kinetic effect of systematic variation of the π-donor/acceptor groups on aryl ring substituents at C and N in the pyrazoline ring is consistent with a pericyclic process for dyotropy of these compounds, but not with rearrangement mediated by biradicals resulting from single H atom transfer in the rate-limiting step. Computer modelling of the transition state for dyotropy of these compounds is also consistent with a thermal, orbital symmetry conserved pericyclic reaction. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: intramolecular thermal ($4\sigma + 2\pi$) dyotropy; kinetic isotope effects; limiting barrier parameters; quantum tunnelling; 2H transfer processes

The thermal isomerizations depicted for the *endo* constrained trienes **1, 3** and **5** into their aromatic counterparts **2**[1], **4**[2] and **6**[3] by transfer of two H atoms on to the proximate receptor π-bond are examples of uncatatalysed intramolecular dyotropic rearrangements as defined[4] following unambiguous recognition of the process.[1] Intramolecular 2H group transfer is an orbital–symmetry allowed thermal process[5] analogous to 2H exchange in the degenerate ethane + ethene $\rightleftharpoons$ ethene + ethane intermolecular process which has $(4n + 2)$-electron transition-state MOs of aromatic character, where, however, a substantial barrier (50–70 kcal mol^{-1}) is predicted by theory.[6,7] Dyotropy of triene **1, 3** and **5** (Scheme 1) and close analogues is an irreversible, exothermic, quantitative process free from side reactions and very fast for **5** ($\rightarrow$**6**) with an estimated activation energy of $\leq$18 kcal mol^{-1}, but more generally characterized by an E_a in the range 25.1–28.3 kcal mol^{-1} for chlorine-substituted 2H receptor π-bond analogues *e.g.* **1** ($\rightarrow$**2**) and **3** ($\rightarrow$**4**);[1–3,8] (E_a values of *ca* 28 kcal mol^{-1} are also found for compounds like **1** but having a vinyl ether ClC = COR receptor π-bond[2a,3,8]). The relative reactivity of trienes **1, 3** and **5** is such that **5** is unisolable at room temperature, whilst **1** only slowly transforms into **2** at *ca* 25 °C with a mean k_1 for dyotropy in decalin solution of 7.10×10^{-8} s^{-1} measured at 26.6 °C. Triene **3** is less reactive still; kinetic data extrapolated to 26.6 °C for comparison with **1** shows that its rate of conversion into **4** is nearly 80 times slower than dyotropy of **1** into **2**.[8] Significantly, dyotropomer **2** is the sole product formed on long-term storage of crystalline **1** at 20 °C.[3,8]

The measured exothermicity (ΔH_i) for dyotropy of triene **3** is 22.63 ± 0.41 kcal mol^{-1} and from this, $E_{a,0}$, the barrier for the *thermoneutral*, *single-step* process can be calculated[2a] to be 39.6 kcal mol^{-1}. This value of $E_{a,0}$ is in very good agreement with *ab initio* calculations for the thermoneutral dyotropy of the parent hydrocarbon **7** $\rightleftharpoons$ **8** (Scheme 2) carried out by Houk *et al.*[9] which yield $E_{a,0}$ = 39.9 kcal mol^{-1} for the concerted (but not necessarily synchronous) process. These calculated data for the

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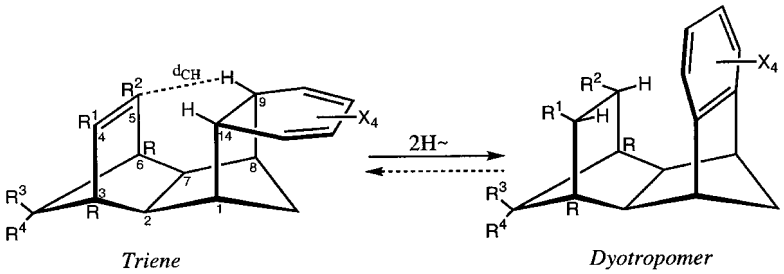


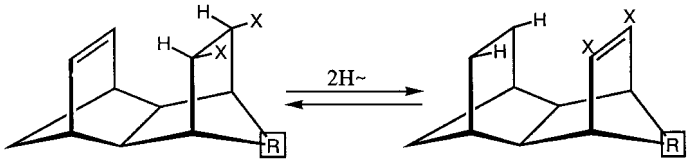
Triene *Dyotropomer*

1 $R = R^1 = R^{1\text{-}4} = X = Cl$ ⟶ **2**

3 $R = R^{1,2} = X = Cl\ R^{3,4} = H$ ⟶ **4**

5 $R = R^{1\text{-}4} = H\ X = Cl$ ⟶ **6**

Scheme 1.



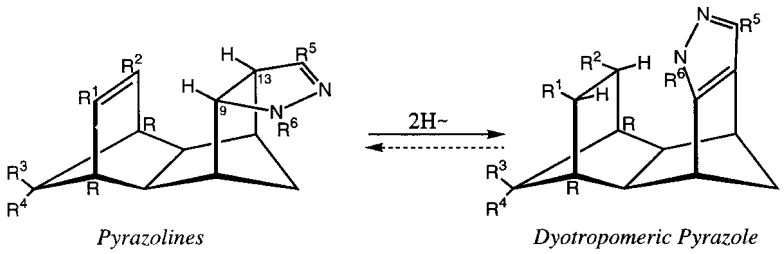
Dyotropic Equilibria

7 $R = CH_2\ X = H$ ⟷ **8**

9 $R = O\ X = CO_2Me$ ⟷ **10**

11 $R = CH_2\ X = SO_2Ph$ ⟷ **12**

Scheme 2.



Pyrazolines *Dyotropomeric Pyrazole*

13 $R = R^{1\text{-}4} = Cl\ R^{5,6} = p\text{-}ClC_6H_4$ ⟶ **14**

15 $R = R^{1\text{-}4} = Cl\ R^{5,6} = p\text{-}MeC_6H_4$ ⟶ **16**

17 $R = R^{1,2} = Cl\ R^{3,4} = H\ R^{5,6} = Ph$ ⟶ **18**

19 $R = R^{1\text{-}4} = H\ R^{5,6} = p\text{-}ClC_6H_4$ ⟶ **20**

Scheme 3.

thermoneutral reaction also compare favourably with $E_{a,0}$ estimated for the dyotropic equilibrium of furano compounds **9** ⇌ **10** in experiments by Vogel *et al.*[10] and calculated from data supplied by Paquette *et al.*[11] for *syn*-sesquinorbornene derivatives, **11** ⇌ **12**. These experimental data yield 36–39 and 36.5 kcal mol^{-1}, respectively, for $E_{a,0}$. Clearly, for trienes **1, 3** and **5** and their analogues, π-bond saturation and aromatization are important barrier-lowering features of their irreversible dyotropy.

Analogous reactions are found for the pyrazolines **13** → **14, 15** → **16** and **17** → **18** (Scheme 3), which exhibit clean kinetic behaviour in oxygen-free decalin solution (*cf.* Fig. 1), but here the observed E_a values are higher and cover a wider range, 31.1–36.7 kcal mol^{-1}, with dyotropic rate-constants 10^2–10^3 times smaller at comparable temperatures than for the trienes **1**, etc.[2a,8] In analogy to triene **5**, which has an unsubstituted receptor π-bond, dyotropy of norbornene-unsubstituted pyrazoline **19** is considerably faster, by 15-fold, compared with, e.g.,

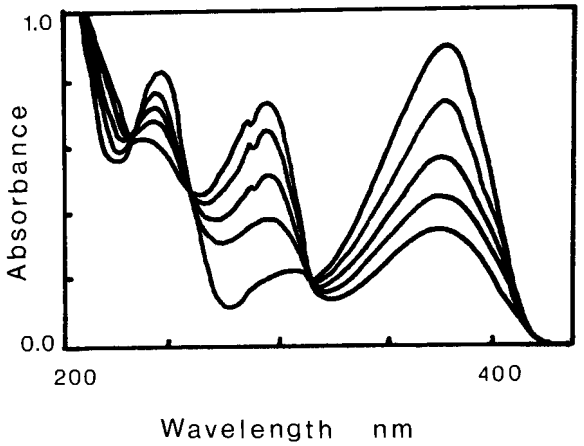
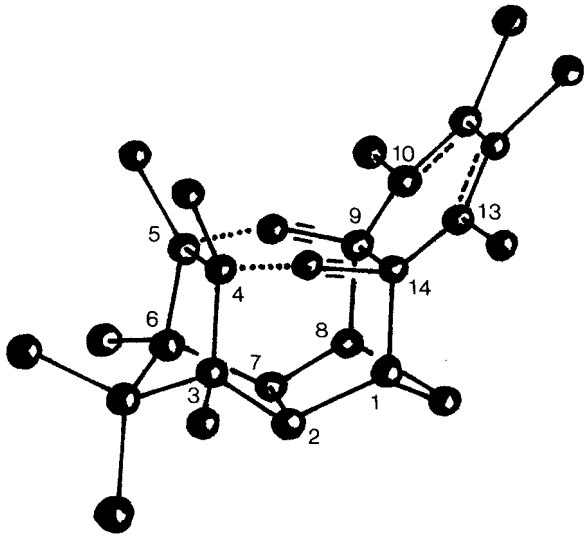


Figure 1. Typical unimolecular kinetic behaviour of 10,12-diarylpyrazolines in degassed N_2-purged decalin solution: compound **25**, 196°C, 1 h intervals, λ_{max} pyrazoline 372.5 nm, pyrazole 292–293 nm

pyrazoline **13**, but the effect is not so dramatic as seen for triene **5** where the rate-differential k_1 (**5**): k_1 (**1**) is $\geq 2 \times 10^5$ at 36°C. The rate spread seen for dyotropy of these compounds, normalized to the rate for the fastest example observed, **5**→**6**, is extraordinarily wide, *viz*, 10^{12}–10^{13} for the ratio k_1 (max):k_1(min) observed, and invites interest in the detailed reaction mechanism; is it a concerted (if asynchronous) process as allowed by theory[5,6,7] and some of the experimental data (as above), or can the experimental facts also be accommodated in a two-step process mediated by biradicals?[9,12]

Recent evidence from the solution and solid-state kinetic behaviour of trienes such as **1**[8] provides strong evidence that reactive intermediates are not involved in their dyotropy; differential solvent effects on the dyotropic rate for the triene systems and small aryl-ring substituent kinetic effects in the pyrazolines analogous to **13** do, however, indicate development of polarity in the transition state, suggestive of asynchronicity in the 2H



Bond	Interatomic distances (Å)		
	AM1	PM3	^{2}H-**1** crystall-data
C(14) — H(14) = C(9) — H(9)	1.327	1.356	1.093(2), 1.095(2)[a]
C(5) — H(9) = C(4) — H(14)	1.421	1.453	2.50(5), 2.35(5)[a]
C(4) — C(5)	1.448	1.441	1.341(2)[a]
C(9) — C(14)	1.488	1.479	1.569(2)[a]
C(9) — C(5) = C(14) — C(4)	2.595	2.626	3.041(7), 3.072(7)
C(12) — C(13) = C(10) — C(11)	1.371	1.363	1.343(2)[a]
C(13) — C(14) = C(10) — C(9)	1.447	1.449	1.507(2), 1.503(2)[a]
C(11) — C(12)	1.442	1.434	1.474(2)[a]
	Interatomic angles (°)		
C(14) — H(14) — H(4) = C(9) — H(9) — C(5)	141.58	138.39	119.3, 127.3
C(1) — C(14) — H(14) = C(8) — C(9) — H(9)	101.46	102.26	112.4, 111.5[a]
H(9) — C(9) — C(14) = H(14) — C(14) — C(9)	103.51	104.35	111.6, 110.3[a]

[a] Neutron diffraction data, 15 K. For a closely related protio-isotopolgue of [^{2}H]-**1**, neutron diffraction data indicate that C(14) — H(14) and C(9) — C(9) are identical with relevant C— D bond lengths within a maximum difference of 0.005 Å.

Figure 2. Computer modelling of transition state for dyotropy of triene **1** (→ **2**), AM1 and PM3 methods and comparison of parameters with crystallographic data for [^{2}H]-**1**[16]

Table 1. Calculated mean temperature dependence of primary deuterium kinetic isotope effect for pryazolines **13** and **15** and triene **1**[a]

T (K)	503.1	493.1	483.1	473.1	463.1	453.1	443.1	433.1	423.1	413.1	403.1
10^3(1/K)	1.988	2.028	2.070	2.114	2.159	2.207	2.257	2.309	2.363	2.421	2.481
Pyrazolines **13**											
$\mathrm{Ln}(k_1^{2H}/k_1^{2D})$	1.407	1.464	1.523	1.586	1.648	1.716	1.788	1.861	1.937	2.020	2.104
Pyrazolines **15**											
$\mathrm{Ln}(k_1^{2H}/k_1^{2D})$	1.586	1.607	1.629	1.652	1.675	1.700	1.726	1.753	1.781	1.812	1.843
T (K)	398.1	388.1	378.1	368.1	358.1	348.1	338.1	328.1	318.1	308.1	298.1
10^3(1/K)	2.512	2.577	2.645	2.717	2.792	2.873	2.958	3.048	3.144	3.246	3.354
Trienes **1**											
$\mathrm{Ln}(k_1^{2H}/k_1^{2D})$	1.903	1.958	2.017	2.078	2.143	2.213	2.286	2.363	2.445	2.532	2.626

[a] Activation parameters used for calculation, following the method of Melander and Saunders[14] and other data used are those reported.[2a] Graphical plot gradients ($r^2 = 1.000$): **13**, 1.414×10^3; **15**, 0.512×10^3; **1**, 0.859×10^3. Observed PDKIE: **13**, 4.60 ± 0.29 and **15**, 5.33 ± 0.18 at 207.6 °C; **1**, 7.63 ± 0.14 at 108.7 °C.

transfer process. If a two-step mechanism is involved, since *ca* 90% of reactions proceeding by transfer of a single species, H^+, H· or H^-, are believed to involve quantum tunnelling,[13,14] it is expected that tunnelling will contribute to the kinetic behaviour, particularly as these compounds are pre-stressed with respect to receptor sp^2 C atoms and transferring H atoms, which are held closer than the van der Waals distance (2.9 Å). The relevant intramolecular separation (d_{CH}) in these compounds is typically[2a,b,8] 2.4–2.5 Å and similar to d_{CH} in sesquinorbornene (**11**).[11] When tunnelling occurs it is usual to find a large primary deuterium kinetic isotope effect (PDKIE), a steep temperature dependence of the PDKIE and due to curvature in the experimental Arrhenius relationship, a fractional value of the pre-exponential intercepts A^H/A^D, curvature being less pronounced for the heavy atom isotopologue.[15] From PDKIE data for [^{1}H]- and [^{2}H]-triene **1**, all three criteria are indecisive in detecting a tunnelling contribution,[2a,c] and as found later,[8] a linear Arrhenius relationship holds perfectly ($r^2 = 1.000$) over a wide temperature range (0–110.3 °C) with a rate spread of 10^5 for triene [^{1}H]-**1**, suggesting purely 'classical' behaviour, *i.e.* Eyring equation compliance.[14] Some additional evidence for the detailed mechanism of rearrangement of **1** (→**2**) derives from semiempirical AM1 and PM3 computer program modelling of the transition state, which indicates symmetrical structures, with only one imaginary frequency and a tractable transfer of 2H atoms with little deformation of the carbon framework C(1)—C(14) defining the reaction cavity. Transition-state parameters are illustrated in Fig. 2, very clearly indicating its reactant-like structure, the H atoms having advanced towards the receptor C atoms by *ca* 20% of their total trajectory in the transformation of **1** into **2**.

By contrast, from data for [^{1}H]- and [^{2}H]pyrazolines **13**, tunnelling is clearly indicated,[2a,c] with a k_1^{2H}/k_1^{2D} ratio of 4.60 ± 0.29 at 207.6 °C, whilst a steep temperature dependence, $\ln(k_1^{2H}/k_1^{2D})$ *vs* 10^3 K^{-1} of 1.420 *(Table 1)*, delivers a kinetic ratio k_1^{2H}/k_1^{2D} of 28.2 at 25 °C (*cf.* trienes **1**, 13.8 at 25 °C). In addition, for the pyrazolines **13**, the intercept ratio A^{2H}/A^{2D} is 0.245 ± 0.143. Since chlorine substituent changes in the norbornene ring proximate to the receptor π-bond result in parallel kinetic effects which are virtually identical in magnitude for both trienes, *e.g.* **3** and pyrazolines **17** (and for other analogous pairs of partially dechlorinated compounds) at the same temperature,[8] it is reasonable to assume that transition-state features for the pyrazolines are similar to those calculated for triene **1**. On this basis, and the general postulate that only one normal vibrational mode acquires an imaginary frequency in a transition state, the C— H/C— D zero-point energy difference is not simply doubled for the 9,13-$^2H_2$-isotropologue of pyrazoline **13** compared with the 9,13-$^1H_2$-species[17] as tacitly assumed.[2,8] The difference in the mean activation energies ($E_a^{2D} - E_a^{2H}$) for the isotopologues of **13** is considerable, 2.80 kcal mol^{-1}, reflecting the substantial tunnelling contribution to the kinetic behaviour of the protio compound. The magnitude of this difference in activation energies will also be influenced by the exothermic nature of the process for which relevant C—H/C—D vibrations may not entirely vanish in a reactant-like transition-state.[15] It is revealing that none of the criteria for a tunnelling contribution are met for the close analogue **15** of pyrazoline **13**. For **15** the measured value of E_a, 33.2 kcal mol^{-1}, is *larger* than the apparent value of E_a for **13**, and yet **15** rearranges faster than **13** by a factor >2.[2a] It is therefore possible that E_a for the behaviour of pyrazoline **15** is close to a critical value for the onset of significant tunnelling, which must be a little larger than 33 kcal mol^{-1}.[8] Analysis of the barrier parameters for pyrazoline **13** by fitting of the PDKIE data to the Bell equation[18b] fully corroborates this conclusion.

As discussed by Melander and Saunders[14] and using their terminology, when tunnelling occurs, the Arrhenius equation is modified by a coefficient, Q_H (or Q_D), which represents a temperature-dependent enhancement of the 'true' (semiclassical) rate constant, k_1(SC), due to the tunnelling contribution and k_1(obs) is actually the value of, e.g., $Q_H A\exp(-E_a/RT)$. Using the Caldin–Mateo

Table 2. Semi-classical rate constants k_1(SC) for dyotropy, $k_1{}^{2H}$(SC) = $k_1{}^{2H}$(obs.)/Q_H,$k_1{}^{2D}$(SC) = $k_1{}^{2D}$(obs.)/Q_D, where $Q_{H(D)}$ are tunnelling coefficients.[a]

Compound	T (°C)	$10^5 k_1{}^{2H(2D)}$(obs.)	$Q_{H(D)}$	$10^5 k_1{}^{2H(2D)}$(SC)
Triene [^{1}H]-**1**	75	2.34	1.562	1.49(8)
	79.8	3.85	1.542	2.49(7)
	82.2	4.85	1.532	3.16(6)
	84.8	6.26	1.522	4.11
	87.7	8.46	1.510	5.60
	90.0	10.6	1.502	7.05(7)
	95.0	16.6	1.484	11.1(9)
	96.0	18.4	1.480	12.4
	99.9	26.2	1.467	17.8(6)
Triene [^{2}H]-**1**	98.7	3.03	1.203	2.51(9)
	104.1	5.08	1.197	4.24
	108.7	7.73	1.191	6.49
	110.7	9.42	1.189	7.92
	114.1	12.6	1.186	10.6
	115.7	14.8	1.184	12.5
	118.9	19.5	1.180	16.5
	123.8	29.9	1.175	25.4
Pyrazoline [^{1}H]-**13**	183.1	1.87	3.730	0.501
	185.7	2.34	3.651	0.641
	190.0	3.14	3.528	0.896
	193.0	3.94	3.448	1.14
	196.7	5.15	3.356	1.53
	199.5	6.28	3.290	1.91
	207.6	11.04	3.116	3.54
Pyrazoline [^{2}H]-**13**	195.1	0.965	1.684	0.573
	199.9	1.34	1.665	0.805
	205.0	2.05	1.645	1.24(6)
	207.6	2.39(8)	1.635	1.46(7)
	215.0	4.26	1.608	2.64(9)
	217.0	4.92	1.601	3.07
	220.0	6.02	1.591	3.78
	224.9	8.54	1.575	5.42

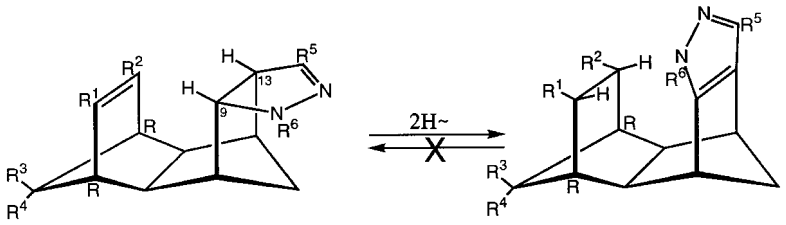
[a] Kinetic data observed refer to N_2-purged degassed decalin solutions. Values of k_1 were usually obtained from five composition–time determinations at each temperature.[2a] Total number of log[rel.conc]–time data-points collected (non-correlating data points neglected) and standard deviations, $(\sigma_{n-1})/k_1 \times 100$, range %, average %:[^{1}H]-**1**, 50, (0), ±0.5–2.47%, ±1.38%; [^{2}H]-**1**, 40, (2), ±0.33–3.16%, ±1.78%; [^{1}H]-**13**, 33, (2), ±0.66–4.98%, ±2.29%; [^{2}H]-**13**, 37, (0), ±1.41–4.53%, ±2.73%.

Table 3. Observed and tunnelling-corrected activation parameters for dyotropy, (E_a, kcal mol^{-1})

Compound	E_a(obs.)	E_a(SC)	Log A(obs.)	Log A(SC)
[^{1}H]-**1**	25.0(7) ± 0.1	25.70 ± 0.1	11.09 ± 0.0(6)	11.29 ± 0.1
[^{2}H]-**1**	26.7(7) ± 0.1	26.9(4) ± 0.1	11.20 ± 0.0(5)	11.25 ± 0.0(4)
[^{1}H]-**13**	31.4(3) ± 0.2	34.6(5) ± 0.1	10.32 ± 0.0(8)	11.29 ± 0.1
[^{2}H]-**13**	34.2(3) ± 0.3	35.2 ± 0.2	11.93 ± 0.1(4)	11.20 ± 0.1(7)

computer program[19] we have evaluated Q_H and Q_D for the triene istopologues [^{1}H]- and [^{2}H]-**1** and for the analgous pairs of istopologues of pyrazolines **13** and **15**.

The semi-classical rate constants k_1(SC) are derived from k_1(SC) = k_1(obs)/$Q_{H(D)}$ and the results are given in *Table 2*. From these data, the Arrhenius equation gives activation energies, E_a(SC), corrected for tunnelling and derived 'classical' and observed activation energies are compared in *Table 3*. It is clear that for pyrazoline [^{1}H]-**13**, barrier 'penetration' is occurring 3.22 kcal mol^{-1} below the apex of the classical barrier, $E_a{}^{2H}$(SC) being 34.65 kcal mol^{-1}. It is also very interesting that the mean activation energy difference, [$E_a{}^{2D}$(SC) − $E_a{}^{2D}$(obs)] for the ^{2}H-istopologue of pyrazoline **13** is larger than the experimental uncertainties, remarkable evidence for non-classical kinetic participation even for a 'particle' of larger relative mass compared with H. On the other hand, for pyrazoline **15** and its isotopologue, the measured value of ($E_a{}^{2D} - E_a{}^{2H}$) is ±0.41 kcal mol^{-1} with a ratio of A^{2H}/A^{2D} of 1.73 ± 0.76, strongly suggestive of insignificant tunnelling. Here, fitting the kinetic data to the Bell equation delivers values of Q_H and Q_D as 1.010–



21 - **30**, R = $R^{1\text{-}4}$ = Cl

Group **A**	R^5	R^6	*Rel. Mean Rate, 196° C (Table 4)*
21	Ph	*p*-$MeOC_6H_4$	21.9
22	Ph	*p*-ClC_6H_4	7.20
23	Ph	*p*-$O_2NC_6H_4$	1.00
Group **B**			
24	*p*-$MeOC_6H_4$	Ph	11.6
25	*p*-ClC_6H_4	Ph	10.4
26	*p*-$O_2NC_6H_4$	Ph	6.41
Group **C**			
27	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$	22.6
28	*p*-ClC_6H_4	*p*-ClC_6H_4	6.67
29	*p*-$O_2NC_6H_4$	*p*-$MeOC_6H_4$	15.1
30	*p*-$MeOC_6H_4$	*p*-$O_2NC_6H_4$	3.34
31	Ph	Ph	11.0

Scheme 4.

1.011 and 1.005–1.006, respectively, over the temperature range 185.7–220 °C, confirming the above conclusion. By contrast, the activation energy difference [E_a^{2H}(SC) – E_a^{2H}(obs)] for triene [^{1}H]-**1** although small, 0.63 kcal mol^{-1}, is significantly larger than the experimental uncertainties; the tunnelling contribution is evidently so small (2.5% in E_a terms) as to translate into imperceptible curvature in a typical Arrhenius plot over a temperature range of 110.3 °C. For isotopolgue [^{2}H]-**1**, [E_a^{2D} (SC) – E_a^{2D} (obs)] is of the same order of magnitude as the experimental deviations and consequently no conclusion can be drawn with respect to a tunnelling contribution to the kinetic behaviour here. If present the effect is likely to be smaller than for the [$^1H_2$]-**1** isotopologue.

Fitting of the PDKIE data to the Bell equation also yields the barrier half-width, 0.6 Å for pyrazoline **13**, and this compares favourably with the distance traversed by the H atoms in dyotropic shift, *ca* 1.4 Å established from x-ray and neutron diffraction data for these types of compounds[8,16] and which may be taken to represent the approximate barrier width. Strictly, the Bell tunnelling calculation gives information about the shape of the barrier at the heavy-atom geometry of the reaction cavity where barrier avoidance occurs. This is not the geometry of either the Eyring transition state or the reactant.[17] However, for constrained, rigid frameworks as described here and a reactant-like transition state as predicted for an exothermic process and discussed in detail by Klumpp[15] together with calculations as described above, the inherent approximations in visualizing the barrier parameters are more reasonable than may generally be the case. For the triene [^{1}H]-**1** the data yield a barrier half-width of *ca* 1 Å . The PDKIE analysis therefore quantifies the greater compression effect required in the reaction zone to accomplish dyotropy in the pyrazoline **13** compared with the triene **1**, as reflected in the kinetic divergence between the pyrazolines and trienes in general.

Tunnelling is most likely when the amplitude of the wave function of the transferring 'particle' is of the same order of magnitude as the barrier width, especially at the point of 'penetration,' and a measure of this is the de Broglic wavelength λ_{dB}.[21] For a particle of mass 2 relative to a H atom, with energy of 30 kcal mol^{-1}, λ_{dB} is 0.18 Å (we thank Dr J. Oliva, University of Bristol, for this value). For a parabolic function $V_x = V_0(1\text{-}x^2/a^2)$ taken to represent the barrier,[21] with $V_x = 31.43$ and $V_0 = 34.65$ kcal for **13**, with a barrier half-width, a, of 0.6 Å the region of penetration is 0.18 Å ($-x$) from the

Table 4. Unimoleculor rate-constants, k_1, for dyotropy of pyrazolines **21–30** in N_2-purged decalin, 196 °C[a]

Series **A**	**21**	**22**	**23**	**(31)**
$10^5 k_1$ (s^{-1})	14.7 ± 0.50	4.8 ± 0.10	0.67 ± 0.01	7.40 ± 0.18
Series **B**	**24**	**25**	**26**	
$10^5 k_1$ (s^{-1})	7.78 ± 0.10	6.98 ± 0.20	4.30 ± 0.10	
Series **C**	**27**	**28**	**29**	**30**
$10^5 k_1$ (s^{-1})	15.1 ± 0.30	4.18 ± 0.10	10.1 ± 0.10	2.24 ± 0.22

[a] For the method of synthesis of *novel* pyrazolines **21–27, 29** and **30** and other properties of this class of compounds, see Mackenzie *et al.*[3] These compounds have been fully characterized by C, H, N elemental composition; *m/z*; UV and ^{1}H NMR.[20] Kinetic data are for *five* composition–time determinations for each compound using pyrazoline absorption at 260–275 nm (where isomeric pyrazoles are transparent). For a description of the method used see Mackenzie and co-workers.[2a,3,8] The usual UV procedure proved unsatisfactory for nitro compounds **23, 26** and **30** and k_1 values were obtained by ^{1}H NMR methods using *ca* 20 mg samples dissolved in N_2-purged decalin, solvent blow-off (N_2) and ^{1}H NMR integration of pyrazoline/pyrazole signals ($CDCl_3$–TMS, Jeol Lambda instrument, 300 MHz) No significant products other than the relevent pyrazoles were detected, but it is believed that slight solvent oxidation or product decomposition increased the background absorption in the *ca* 10^{-5} M solution used in the UV assay method; this effect produced standard deviations of ±5–10% in k_1 values compared to ±0.5–4.5% for all other pyrazolines and trienes, of the type described here, which have been investigated.

vertical axis defining the barrier centre. (Using a Gaussian form for the barrier, $V_x = V_0 \exp x^2/, a^2$ yields essentially the same result.) It may be conjectured that when the wave function of the 'particle' extends only half way through the barrier, sufficient 'recognition' of the particle wave function on the product side develops leading to tunnelling. However, it may be coincidence that the penetration distance x and λ_{dB} are nearly identical, especially given the approximations involved.

The absence of significant tunnelling in dyotropy of triene **1** and pyrazoline **15**, together with their relative reactivities, is good evidence that single H atom transfers are not involved. Tunnelling observed in dyotropy of **13** may simply be a consequence of increased barrier height.

The kinetic effect of varying the aryl-ring substitutents, as in the pyrazolines **13** and **15**, is small,[2a] with a rate-difference of *ca* 2 for **15,** > **13** at 196 °C. Useful new information has now been found by comparing diphenylpyrazoline **31** *(Scheme 4)* with two series of compounds in which either N(10)-Ph (series **A**) or C(12)-Ph (series **B**) is replaced with a *p*-anisyl, *p*-chlorophenyl or *p*-nitrophenyl group. In the **A** series (Table 4), pyrazolines **21, 22** and **23** the relative rate ratio k_1 (**21**): k_1 (**31**) is *ca* 2 at 196 °C, the π-donor *p*-methoxy substituent significantly accelerating reaction. When the aryl substituent is a strong π-acceptor as for *p*-nitrophenyl, a more than 10-fold rate reduction is observed, k_1 (**23**):k_1(**31**) being 0.09. In the **B** series of compounds **24, 25** and **26**, substituent variation effects are much smaller. For example, the effect of the *p*-methoxy group in pyrazoline **24** is almost insignificant, k_1(**24**):k_1(**31**) being 1.05, whilst for the *p*-nitro compound **26** the π-acceptor substituent is much less effective in reducing the reaction rate than it is for isomer **23**, with a rate ratio of 0.58 for k_1(**26**):k_1(**31**), k_1(**26**) being more than six times larger than k_1(**23**). A similar reactivity pattern is seen in the **A** and **B** series for the isomeric *p*-chlorophenyl compounds [and in the **A** series for *p*-trifluoromethyl at N(10) where the rate ratio compared with **31** is 0.24, a considerable rate reduction[20]].

A two-step mechanism for dyotropy, mediated by diradicals generated by H atom transfer on to the proximate π-bond from either C(9) or C(13), in the rate-limiting step, appears unlikely also on the basis of these results. Resonance canonical representation of a pyrazoline radical produced at C(9) next to N(10), for example, shows that an identical substituent at N(10) or C(12) should have a similar effect on radical stability and hence reaction rate. Alternatively, since in the reactant-like transition state the pyrazoline is transforming into a 6π aromatic pyrazole utilising the N(10) 2p lone-pair, attenuated electron density on N(10) by, e.g., the *p*-nitrophenyl group in **23** nicely accounts for the observed rate-reduction compared with **31**. As expected from this hypothesis, N(10)-*p*-anisyl substitution is more effective in promoting reactivity, *i.e.* in analogue **21**, than for C(12)-*p*-anisyl compound **24**. Here, polarization of the Ar—C = N element, with relatively large electron density already present on N(11), results in a 'saturation' effect with respect to p–π-donor groups in the aryl ring attached to C(12). This effect rationalizes the very small rate-change seen for pyrazoline **24** compared with **31** and also indicates that significant kinetic effects are more likely to be seen when C(12) is substituted with electron-withdrawing groups—precisely what is observed for *p*-nitrophenyl compound **26**.

The relative rates of rearrangement of pyrazolines **27–30** (series **C**), which have both N(10) and C(12) aryl groups *p*-substituted, are also well accommodated by the above interpretation. For example N(10), C(12)-di-*p*-anisyl compound **27** is only slightly more reactive than the N(10)-mono-*p*-anisyl analogue **21**, whilst the introduction of a second *p*-chlorophenyl group at C(12) in pyrazoline **28** results in the expected, if small, rate reduction compared with N(10)-mono-*p*-chlorophenyl analogue **22**. As seen from Table **4**, k_1(**27**):k_1(**21**) is 1.03 and k_1(**28**):k_1(**22**) is 0.87. For the *p*-anisyl/*p*-nitrophenyl substituted isomers **29** and **30** it is once again clear that it is the N(10)-aryl substituent which largely controls dyotropic reactivity. N(10)-*p*-anisyl-C(12)-*p*-nitrophenyl compound **29** is only about 0.7-fold less reactive in terms of rate ratio compared with mono-N(10)-*p*-anisyl com-

pound **21**. If the substituents are switched round, as in isomer **30**, the N(10) 2p lone-pair depletion effect operates very effectively, reducing reactivity considerably compared with N(10)-*p*-anisyl compound **21**, with a rate ratio k_1(**30**):k_1(**21**) of 0.15.

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