On Intramolecular Dyotropy: Structural Effects on Reaction Rates, Crystal Structure–Molecular Mechanics Correlations and Primary Deuterium Kinetic Isotope Effects.[1] (Parameters for Intramolecular Recognition)

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Previous attempts to prepare the pentacyclic triene **17** for comparison of the rate of intramolecular dyotropy with the kinetics of similar irreversible rearrangements of norbornene ring-substituted analogues had given only dyotropomer **18** with an estimated minimum ratio $k_1(\mathbf{17})/k_1(\mathbf{5}) \sim 2 \times 10^5$ at 36 °C. In the following it is shown that the steric proximity, d_{CH}, of transferring H atoms to receptor sp^2 carbons in the reaction zone cavity together with MM-calculated π-energy differences between dyotropomers can rationalise the large rate enhancement observed for the triene **17** compared with **5** and its analogues. For a series of compounds modelled on **5**, in which d_{CH} variations are quite small, observed differences in dyotropic rate are identified as arising from the interplay of molecular geometry changes and small changes in π-energy at the receptor alkene site occasioned by proximate polar groups, the electronic changes associated with aromatisation of the appended donor-site ring remaining essentially constant across the series. When the electronic energy changes associated with dyotropy for a pair of analogous structures are very closely similar, a rate-spread of *ca.* 10^4 can be identified with a change in d_{CH} of 0.1–0.17 Å. Similar kinetic effects concomitant on small parallel structural variations, virtually identical in relative-rate terms to those in the triene series, are seen in the irreversible dyotropy of a series of analogous pyrazolines modelled on compound **36** and may be likewise rationalised. Kinetic comparisons for a group of aryl-ring substituted analogues of pyrazoline **36** reveal quite modest substituent effects, consistent with reactant-like transition-states for these quantitative, exothermic rearrangements. Inter-series comparison of alicyclic trienes with pyrazolines indicate that when d_{CH} values are essentially identical in representative examples, a rate-differential of 10^2–10^3 between the two series can be identified principally with the differing electronic requirements for triene and (slower) pyrazoline rearrangements. Primary deuterium kinetic isotope effects (k_1^{2H}/k_1^{2D}, $d\ln[k_1^{2H}/k_1^{2D}]/dt$ and especially A_{2H}/A_{2D}) reveal strong evidence for non-classical behaviour especially for pyrazoline **38**.

The remarkable increase in rate for intramolecular chemical change when compared with the intermolecular mode has considerable implications for synthetic methodology[2] and also the detailed course of enzymic catalysis.[3] Compounds which display intramolecular hydrogen dyotropy free from side reactions at conveniently measurable rates, and which furnish crystals suitable for X-ray crystallographic and/or neutron diffraction molecular structure analysis provide suitable models for investigating the interplay of reaction-zone proximity effects and intrinsic steric and electronic energy changes which may accompany the dyotropic process. Information so obtained is also of considerable potential value for understanding the detailed stereochemical requirements for bond-forming and bond-breaking events.[4]

Since the earlier recognition of stereospecific group-transfer of two hydrogen atoms to a proximate π-bond (the receptor) in an exothermic, irreversible and non-catalysed quantitative $(4\sigma + 2\pi)$ thermal rearrangement[5a,b] (Scheme 1), there have been relatively few other reports of similar or related group-transfers.[6] Contrasting with our work and the recent work of Grimme *et al.*[6d] disclosing an example of $(4\sigma + 6\pi)$ dyotropy are examples of thermoneutral, reversible dyotropy, *e.g.*, **13** ⇌ **14** recognised by Vogel *et al.*,[7] and more recently, *e.g.*, **15** ⇌ **16** and many analogous equilibria which have been the subject of detailed investigations by Paquette *et al.*[8a,b] For a series of compounds having the structural features of **15** and **16** and which exhibit reversible intramolecular dyotropy uncomplicated by perceivable electronic perturbations, Paquette *et al.*[8a] have observed a kinetic spread of 10^4 for a modulation of rather more than 0.1 Å in d_{CH}, the crystallographically measured internuclear separation of sp^2-C atom receptor-sites and H atoms transferred, whilst we[9] and Prinzbach *et al.*[10] have observed a remarkable rate-enhancement for dyotropy with triene **17** (→**18**), the norbornene-substituted analogue of triene **5** (Scheme 1). Triene **17** could not be isolated at room temperature; instead, attempted synthesis by exposure of hexadechloro-**1** to tetrachlorothiophene dioxide (TCTD) at 25 °C gives instead its (known)[5a] dyotropomer **18**. Kinetic measurements indicate that at 36 °C, k_1 for dyotropy of **17** (→**18**) is at least 4×10^{-2} s^{-1}. By contrast, triene **5** exhibits only very slow detectable dyotropy at 20–25 °C (*cf.* Table 1) but suitable extrapolation using the data in Table 2 gives the rate-ratio, **17**:**5** ≅ 2×10^5 at 36 °C.[9] Clearly, substituents on the norbornene receptor element have a profound effect on the rate of the dyotropic process, and without prejudice to alternative

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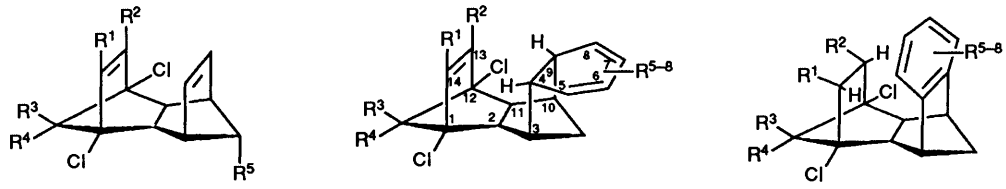
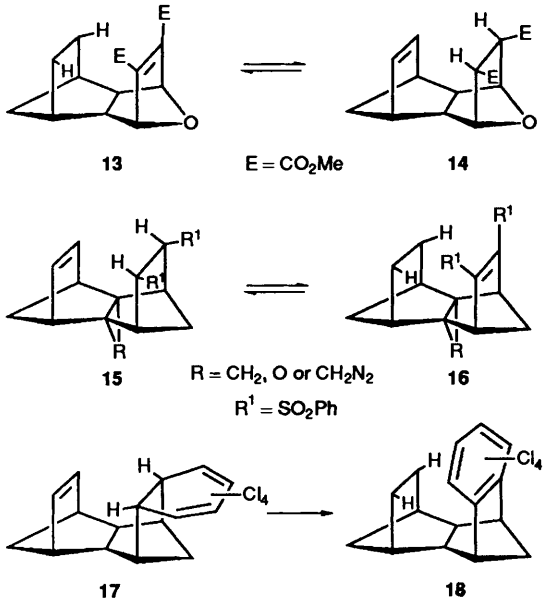


$R^5 = H$

1 $R^{1-4} = Cl$ —i,ii,iii→ **5** $R^{5-8} = Cl$ —iv→ **9** $R^{5-8} = Cl$
[**2** $R^{1-4} = Cl$ **6** $R^{5-8} = Aryl$ **10** $R^{5-8} = Aryl]^a$
3 $R^1 = OEt$; $R^{2-4} = Cl$ **7** $R^{5-8} = Cl$ **11** $R^{5-8} = Cl$
4 $R^{1,4} = H$; $R^{2,3} = Cl$ **8** $R^{5-8} = Cl$ **12** $R^{5-8} = Cl$

Scheme 1 *Reagents:* i, $C_5Cl_4(OMe)_2$; ii, H^+/H_2O; iii, heat, $-CO$; iv, heat
[a] Cyclopentadienone addition, heat, $-CO$



13 $E = CO_2Me$ **14**

15 $R = CH_2$, O or CH_2N_2 **16**
$R^1 = SO_2Ph$

17 **18**

interpretations[8c] the information obtained in this respect[9] points to the pericyclic character of these rearrangements.

To address the question of the origins of this remarkable rate-acceleration observed for triene **17** compared with analogue **5**, we have made a number of compounds, *e.g.*, **22**, **23** and **24** and their thermal dyotropomers **25**, **26** and **27** (Scheme 2), closely similar to triene **5** and its dyotropomer **9**, in which the π-elements might be expected to be kept essentially constant in structure, but not necessarily in electronic character especially with respect to the norbornene receptor site. In the group of trienes **22–24**, relevant d_{CH} values are also expected to be slightly modulated concomitant with bridge-methylene dehalogenation. The X-ray and neutron-diffraction derived structural features of these compounds, together with MM calculated strain-energies (E_s) and π-energies (E_π) for pairs of dyotropomers suggest that correlations can be made between these molecular properties and rate of dyotropic rearrangements, as well as with d_{CH}.

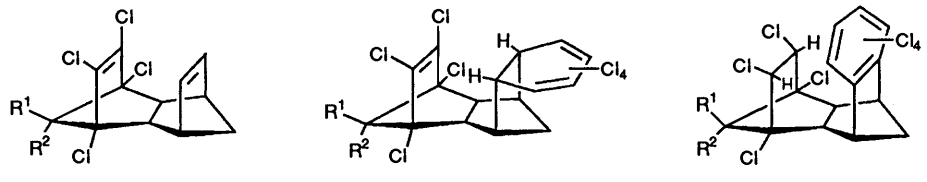
Table 1 Unimolecular rate constants for dyotropy, k_1, alicyclic trienes[a]

Compound	T/°C	$k_1/10^{-5}$ s^{-1}
5	79.8	3.85
	82.2	4.85
	84.8	6.26
	87.7	8.46
	90.0	10.6
	95.0	16.6
	96.0	18.4
7	99.8	1.68
	105.0	2.87
	107.0	3.46
	109.8	4.59
	115.0	7.32
	115.2	7.72
	120.0	11.3
22	100.0	2.87
	105.2	4.75
	110.6	7.71
	115.0	11.5
	120.0	18.5
23	100.0	3.29
	105.2	5.40
	110.6	8.72(6)
	115.0	13.3
	120.0	21.8
24	100.0	1.34
	105.2	2.23
	110.6	3.71
	115.0	5.80
	120.0	9.34

[a] Total number of log [comp.]/time data points collected, 152 (non-correlating data-points neglected, 1). Standard deviations:

$$\frac{\sigma(n-1)}{k_1} \times 100, \pm 0.5\text{–}3.05\%, \text{average} \pm 1.36\%.$$

Data-points collected in random replicate experiments, 29. Average difference isothermal k_1, values ±2.03%.



19 $R^1 = H$; $R^2 = Cl$ —i→ **22** —ii→ **25**
20 $R^1 = Cl$; $R^2 = H$ **23** **26**
21 $R^1 = R^2 = H$ **24** **27**

Scheme 2 *Reagents:* i, tetrachlorothiophene dioxide, $CHCl_3$, 61 °C, 72 h; ii, heat

Table 2 Activation parameters for dyotropy–alicyclic trienes

Compound	ΔE_a[a]	$\Delta H^{\ddagger}$[a]	$\Delta S^{\ddagger}$[b]	$\Delta G^{\ddagger}$[a]	log A
5	25.07 ± 0.17	24.48 ± 0.17	−9.76 ± 0.09	27.39	11.09 ± 0.10
7	27.69 ± 0.35	27.08 ± 0.35	−8.22 ± 0.14	29.53	11.43 ± 0.20
22	26.84 ± 0.28	26.42 ± 0.28	−9.00 ± 0.13	29.10	11.26 ± 0.16
23	27.41 ± 0.49	26.82 ± 0.45	−7.67 ± 0.18	29.11	11.55 ± 0.28
24	28.33 ± 0.31	27.74 ± 0.30	−6.99 ± 0.11	29.82	11.70 ± 0.18

[a] kcal mol^{-1}. [b] cal mol^{-1} K^{-1} converted from data expressed in kJ and J. Deviations are standard deviations.

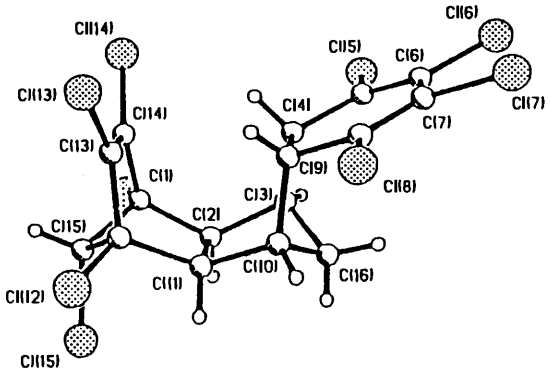


Fig. 1 Computer-generated X-ray crystallographic perspective representation of triene **22**

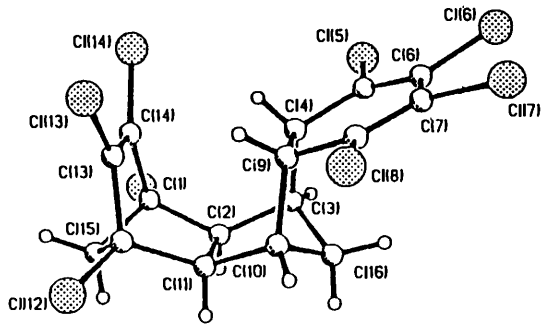


Fig. 2 Computer-generated X-ray crystallographic perspective representation of triene **24**

X-Ray Structural and Kinetic Results for Trienes Depicted in Schemes 1 and 2.—The structural detail revealed by the molecular framework of trienes **22**, **24** and their dyotropomers **25** and **27** (Figs. 1–3) shows that there is some distortion in the solid state for all these compounds, with a consequent small inequivalence of the two d_{CH} values across the reaction-zone (Table 3). (A similar effect has been seen in the compounds studied by Paquette *et al.*[8a]) The averaged d_{CH} is therefore used in the following discussion. The X-ray and neutron diffraction data also show that the inter-cavity d_{CC} separations are much less sensitive to this effect, the ethano- and etheno-bridge planes remaining nearly parallel. Another relevant observation concerns the near-identity of these d_{CC} distances in each of the dyotropic isomer-pairs **22**, **25** (Fig. 3) and **24**, **27**, the pairs of dyotropomers also displaying closely similar d_{CH} values. OFIT[11] computer-generated superposition of the lattice structures of these and other pairs of dyotropomers shows that their etheno- and ethano- and methylene bridges almost coincide spatially (*e.g.*, Fig. 3), the maximum deviation of planes defined by these structural elements and their connections to the common ring-junction [C(2)–C(11)] being ±3°. From this and other information, the average H nuclear traverse between alternative loci during dyotropic 2 H transfer is estimated to be 1.7 Å.

The irreversible, quantitative dyotropy observed for the series of trienes depicted in Schemes 1 and 2, is well illustrated for, *e.g.*,

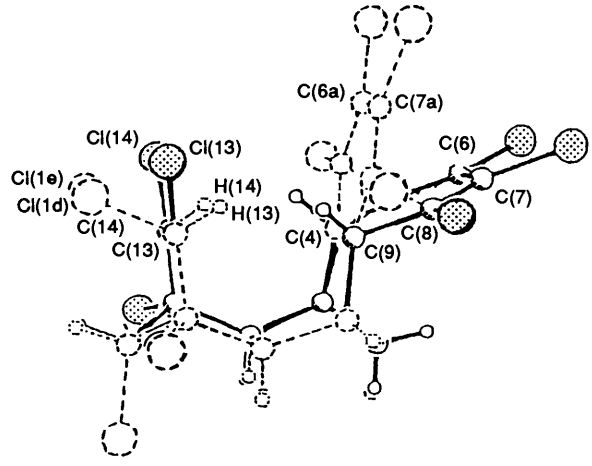
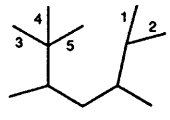


Fig. 3 OFIT computer-generated superposition of X-ray models of triene **22** and its dyotropomer **25**

Distance/Å		Angles between planes	
C(4)–C(4a)	0.119	Planes (1) and (2)	55.9°
C(5)–C(5a)	1.273	Planes (3) and (4)	62.6°
C(6)–C(6a)	2.317	Planes (3) and (5)	119.0°
C(7)–C(7a)	2.262	Planes (4) and (5)	56.4°
C(8)–C(8a)	1.193		
C(9)–C(9a)	0.067		
H(4)–H(14)	1.680		
H(9)–H(13)	1.759		
Cl(13)–Cl(1d)	1.403		
Cl(14)–Cl(1e)	1.433		



7, which melts exothermically near 180 °C and re-solidifies to give essentially pure dyotropomer **11**.[5a] The degree of exothermicity is illustrated for triene **24**. Differential scanning calorimetry (DSC) reveals a transition at 184 °C with ΔH = −22.63 ± 0.41 kcal mol^{-1} (with an endothermic transition, 6.58 kcal mol^{-1} at 240 °C, the dyotropomer m.p.).*

The notable exothermicity characterising dyoptropy for these compounds, associated with concomitant aromatisation, implies reactant-like (asymmetric) transition states, but in which the donor and acceptor carbon atoms defining the reaction zone are, to some extent, connected together by the H atoms in what is almost certainly a non-linear 2 H transfer process. It is also very likely that the relevant C–H bonds are affected by skeletal vibrational modes, which also have the effect of compressing the reaction-zone, forcing the transferring H atom closer to the acceptor sp^2-C atoms.[12] During the course of reaction, the trienes, transforming into aromatic compounds, are clearly folding inwards (Fig. 3 plane 2 moving into plane 1), the largest framework nuclear motion being associated with this process. All these effects imply transition-states more ordered

* We thank Dr. P. Gates and Dr. W. Xiaoping, Royal Holloway and Bedford New College, University of London for this measurement. (1 cal = 4.182 J.)

and 'stiffer' than the ground state molecules, and which is reflected in the thermochemical parameters (Table 2), particularly the Arrhenius pre-exponential factor, A, and the negative $\Delta S^{\ddagger}$ terms [and $A \cong k_B T_e/h \exp(\Delta S/R)$]. Concordant with a process affected by the above transition-state features the A-values (1.23–5.01 × 10^{11} s^{-1}) are significantly smaller than is observed for many unimolecular reactions, where A is often of the order of 10^{13}–10^{14} s^{-1}, but are similar in magnitude to values found for, *e.g.*, intramolecular [1,5]-sigmatropic H-transfers[13] a related process with similar transition state contraint.

All the above observations lead to the expectation that changes in ΔH_f, reactant strain energy differences E_s and especially the order of magnitude of reactant-product π-energy differences ΔE_π—in addition to modulation of d_{CH}—play a critical role in determining isomerisation rates for these, and related classes, of compound. MM calculations have therefore been carried out for trienes **5**, **7**, **17**, **22**, **23**, **24** (and **30**, see later) and their respective aromatic dyotropomers for provision of thermochemical data, for comparison of calculated d_{CH}, d_{CC} values with experimental values, and to obtain the latter parameters otherwise unobtainable experimentally, *e.g.*, for trienes **5*** and **17**; relevant data are presented in Table 3.[14] Relatively good agreement for experimental and calculated average d_{CH} values for **22** and particularly the less distorted molecule **25**, give grounds for confidence in the calculated d_{CH} value in elusive triene **17**, 2.38 Å, compared with average experimental d_{CH} values of 2.45–2.54 Å for, *e.g.*, trienes **22** and **24**. In particular the attenuated internuclear C–H separation d_{CH} for **17**, taken together with the significantly larger ΔE_π value compared with that for rearrangement of each of trienes **5**, **7**, **22**, **23** and **24** into their respective dyotropomers and a decrease in E_s for aromatic dyotropomer **18** compared with its progenitor **17**, conspire to increase the exothermicity of rearrangement and to deliver exceptional reactivity for this compound.

Like their analogues in Scheme 1[9] trienes **22**, **23** and **24** (Scheme 2) exhibit clean dyotropy and are kinetically well behaved. Unimolecular rate constants, k_1, measured at 100 °C (Table 1) compared with k_1 for triene **5** at this temperature show only a small kinetic spread in comparison with the exceptional triene **17**, relative-rate-ratios for **5**:**23**:**22**:**24** being **17**:**2**:**2**:**1**. The crystal structure data for trienes **22** and **24** (Table 3) reveal a difference of 0.07–0.10 Å in d_{CH} for **22** (average 2.54 Å) compared with **24** [average 2.47 Å (2.39 Å, neutron data, 15 K)]. Triene **24** does have a significantly smaller d_{CH} compared to its analogue **22** and might be expected to rearrange noticeably faster than is observed, suggesting the operation of other decelerating factors. One possibility arises from the suggestion that electron density in the reaction zone associated with the acceptor sp^2-C atoms may also contribute to rate control for intramolecular dyotropy.[10,15] Such an effect would be modulated by sp^2-C pyramidalisation at C(13)–C(14) in, *e.g.*, trienes **22** and **24**. In fact, for **24** C(13) and C(14) Cl atoms tilt 1.8° in the *endo* direction, *i.e.*, into the cavity, implying *exo* pyramidalisation at C(13) and C(14) and a reduction in reaction-zone π-density compared with **22**; for **22**, pyramidalisation is in the opposite, *endo* direction (π-tilt 1.6°) with a corresponding increase in π-density. The steric proximity effects (d_{CH}) and π-density modulation induced by sp^2-C pyramidalisation thus operate in the opposite sense in both trienes **22** and **24**; their combined effect for each species could account for a levelling in k_1 for these triene analogues.

The exothermicity across a range of compounds undergoing an identical transformation should reflect itself in perceivable rate-differences. It is reasonable to suppose that exothermicity will be strongly affected by changes in π-energies due to receptor sp^2-C saturation and diene ring aromatisation. For the group of trienes **5**, **23** and **24** with nearly constant (isoapostatic)† d_{CH} (2.46–2.47 Å), a linear correlation of dyoptropic rate with ΔE_π is clearly seen with $\ln k_1 = -(401.82 + 9.29\ \Delta E_\pi) \pm 0.21$, but triene **22** deviates significantly (by 10%). For exothermic rearrangements having reactant-like transition states, differences in reactant ground-state strain-energy E_s for otherwise similar molecules should also be reflected in rate differences, and indeed the correlation of $\ln k_1$ with E_s for the triene group **5**, **23** and **24** is again linear with $\ln k_1 = -(21.96 - 0.122\ E_s) \pm 0.24$; again triene **22** shows a larger deviation (*ca.* 4.5%). (Whilst the reactant E_s–$\ln k_1$ correlation is mirrored in a similar, (inverse), product E_s–$\ln k_1$ relationship [$\ln k_1 \cong -(21.2\text{–}0.107\ E_s)$], there is no simple correlation of $\ln k_1$ with reactant–product strain energy difference, ΔE_s). The reactant-like transition state is clearly seen to be much more sensitive to even small differences in the much larger electronic term, ΔE_π. The consistent deviations for triene **22** towards a 50% smaller k_1 than calculated from these data may then best be rationalised as reflecting the slightly amplified d_{CH} value here (2.54 Å) compared with **5**, **23** and **24** (2.46–2.47 Å).

Unlike triene **5**, the vinylic ether, triene **7** is surprisingly stable at ambient temperature, and also displays anomalies if compared with the virtually isoapostatic triene **24**. At 100 °C the relative dyotropic rate-ratio for **5**:**7** is *ca.* 13. However, in view of the sensitivity of $\ln k_1$ to relative values of ΔE_π, the ΔE_π effect is more favourable for **7**(→**11**) compared with **5**(→**9**) by 0.2 kcal mol^{-1}. The result should be an acceleration of dyotropic rate for **7** compared with **5**, especially since the average d_{CH} (2.46 Å) is identical with that calculated for **5** (and the averaged d_{CC} for **7** is actually smaller than that calculated for **5**).* Moreover, comparison of virtually isoapostatic trienes **7** and **24** (d_{CH} 2.46 and 2.47 Å) yields a rate-ratio near unity at 100 °C despite the relatively more favourable ΔE_π factor for **7**(→**11**) of nearly 0.5 kcal mol^{-1} compared with ΔE_π for **24**(→**27**). In fact E_s(**7**) and ΔE_π**7**(→**11**) have no correlation with the observed kinetic data for the triene group **5**, **23** and **24** despite their isoapostatic d_{CH} values, leading to the conclusion that some other so-far unquantified factor operates in decelerating dyotropy for triene **7**. One possibility is that the vinylic ether sp^2-C receptor-site orbital coefficients, being necessarily different on account of O(2p)–π polarisation, in contrast with their equivalence in the ClC=CCl element common to triene **5** and its analogues, translates into a rate-retarding geometrical distortion in the transition-stage. This effect, likely to be amplified by the observed more serious molecular distortion in the ground state for triene **7** as seen in the crystallographic data, could very well account for the large kinetic difference found for triene **7** compared with **5**, and the loss of correlation with E_s and ΔE_π compared with **5**, (**22**), **23** and **24**.

Dyotropically Active Trienes Derived from Homoisodrin.—Variation in reaction-zone cavity parameters (d_{CH}, d_{CC}) can be achieved in a number of ways.[8a] We sought further to modify d_{CH} in compounds related to those in Schemes 1 and 2, by replacing the methylene bridge with an ethano bridge, utilising homoisodrin **28**[16a] as a dienophile for the capture of TCTD; frustratingly no reaction can be achieved at 20–110 °C!

* We have since obtained low-temperature neutron diffraction data for >98% 4,9-bisdeuterio triene **5** which yield d_{DD} = 2.50(5), 2.35(5) Å (average 2.430 Å) and d_{CC} = 3.072(7), 3.041(7) Å (average 3.057 Å), close to the MM-calculated values of d_{CH} for ^{1}H-**5**, whilst for pyrazoline ^{2}H-**38**, d_{CD} = 2.48(4), 2.53(4) (average 2.509 Å) and d_{CC} = 3.010, 3.051 Å (average 3.030 Å).

† Isoapostatic, 'same distance' from the Greek ιδιο αποσταση.

Table 3 Heats of formation ΔH_f, strain E_S and π-energies E_π

Triene	ΔH_f[a]/ kcal mol^{-1}	E_S/ kcal mol^{-1}	E_π/ kcal mol^{-1}	d_{CC}/Å	d_{CH}/Å	Dyotropomer	ΔH_f/ kcal mol^{-1}	E_S/ kcal mol^{-1}	E_π/ kcal mol^{-1}	d_{CC}/Å	d_{CH}/Å	$\Delta\Delta H_f$	ΔE_π	k_1(100 °C)/ 10^5 s^{-1}
5	49.965	109.74	−272.94	3.14[b]	2.46[b]	**9**	14.407	117.68	−315.28	—	—	−35.558	−42.34	22.5[b]
7	13.30	105.42	−272.73	3.079 2.998	2.548 2.373	**11**	−20.443	109.30	−315.26	3.051[c] 2.955 3.017 3.040	2.260[c] 2.111 2.187 2.188	−33.733	−42.53	1.70
22	46.725	98.18	−273.06	3.074 3.084 3.15[b]	2.489 2.587 2.45[b]	**25**	7.386	102.28	−315.25	3.065 3.064 3.09[b]	2.458 2.443 2.40[b]	−39.339	−42.19	2.87
23	45.90	97.37	−273.10	3.16[b]	2.46[b]	**26**	10.040	104.89	−315.22	—	—	−35.86	−42.12	3.29
24	45.323	86.49	−273.21	3.076[d] 3.104[d] 3.090 3.104 3.16[b]	2.361[d] 2.435[d] 2.46 2.48 2.46[b]	**27**	6.978	91.48	−315.25	3.071[d] 3.090[d] 3.070 3.080 3.10[b]	2.525[d] 2.597[d] 2.478 2.568 2.42[b]	−38.345	−42.04	1.34
17	61.060	70.22	−268.82	3.07[b]	2.38[b]	**18**	27.108	66.74	−315.38	3.073 3.068 3.09[b]	2.426 2.439 2.40[b]	−33.952	−46.56	3 × 10^5[e]
30	43.705	58.76	−268.82	—	2.40[b]	**31**	12.982	58.38	−315.46	3.094[d] 3.106[d] 3.090 3.104	2.556[d] 2.506[d] 2.557 2.628 2.52[b]	−30.723	−46.64	~17[f]

[a] E_π(ene) included in calc. of ΔH_f (HC=CH, −11.94; ClC=CCl, −13.4; ClC=OMe, −11.90 eV. [b] Calculated value. [c] Two independent molecules, J. A. K. Howard, P. Marshall and K. Mackenzie, unpublished work. [d] Neutron diffraction data. [e] Estimated value (4 × 10^{-2} at 36 °C). [f] Estimated value (3 × 10^{-6} at 36 °C).

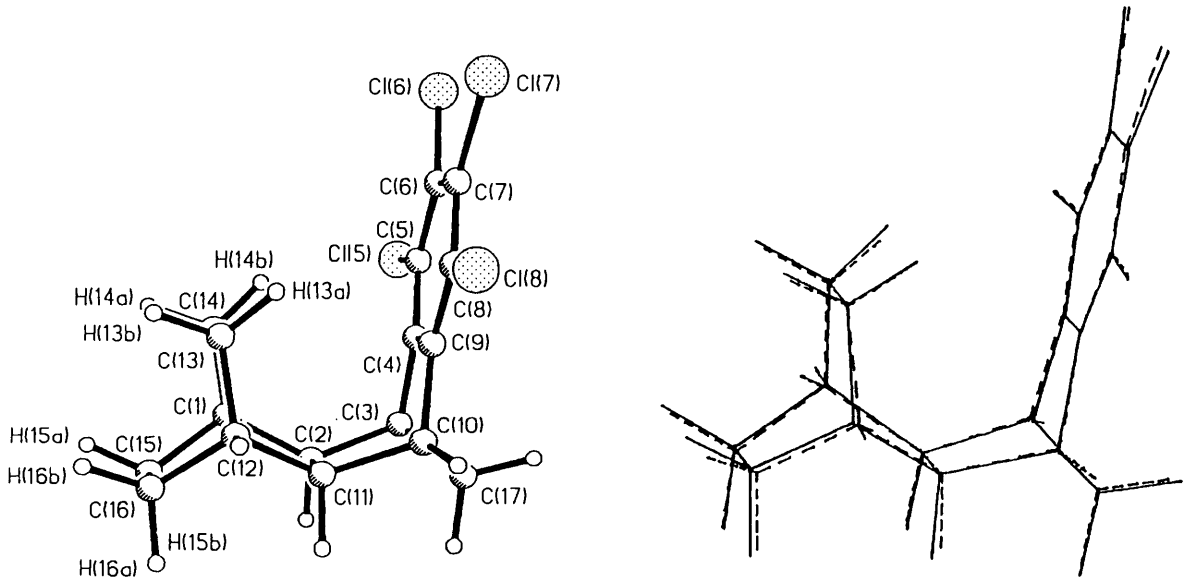
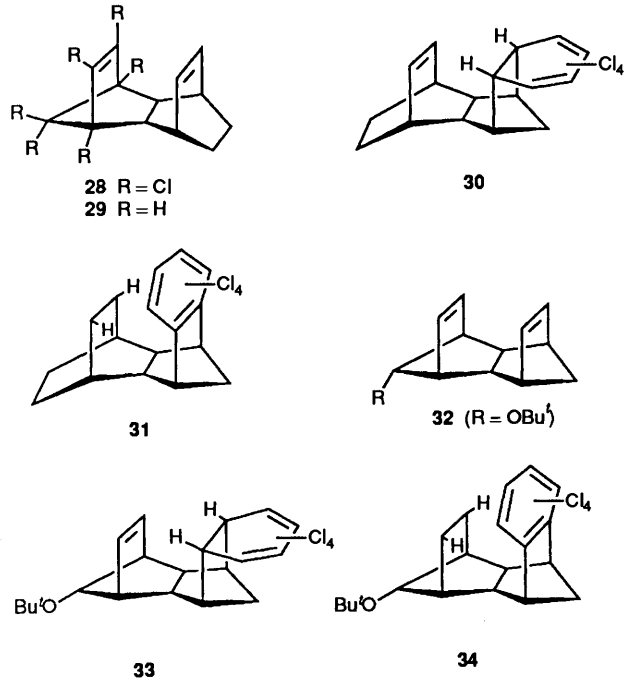


Fig. 4 Computer-generated perspective representation of neutron-diffraction model of dyotropomer **31**, and OFIT computer-generated superposition of X-ray-and neutron-diffraction models of **31**

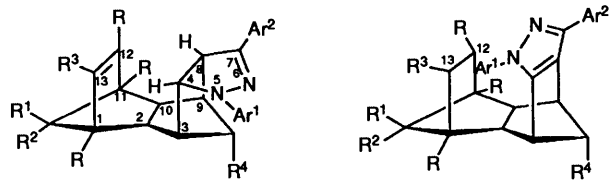


Presumably an insurmountable steric demand which may be identified with the ethano bridge precludes adequate proximity for otherwise highly reactive TCTD.[17] However, dechlorination of homoisodrin **28** by the Bruck, Thomson, Winstein method[18] gives the hyper-active dienophile **29** in high yield. Contact of **29** with TCTD in $CDCl_3$ (each component 0.4 mol dm^{-3} conc.) and ^1H NMR monitoring (36 °C) reveals the rapid formation of triene **30**, and reaction virtually complete in 20 h at 26 °C, with the concomitant appearance of a trace of dyotropomer **31**. At this temperature $\tau_{\frac{1}{2}}$ for triene **30** is 144 h, giving $k_1 = 1.33 \times 10^{-6}$ s^{-1} ($\sim 3 \times 10^{-6}$ s^{-1} at 36 °C) and comparison with the reactive triene **17** gives the rate-ratio **17**:**30** of at least 1.3×10^4. Crystals of unstable triene **30** being unobtainable, use may be made of the d_{CH} and d_{CC} values in its dyotropic isomer **31** for comparison with these parameters for the dyotropomer **18**, derived from **17**. Low-temperature neutron-diffraction studies with **31** * yield accurate values for d_{CH} of 2.556 and 2.506 Å (2.531 Å average, compared with the MM-calculated value of 2.52 Å) and d_{CC} 3.094 and 3.106 Å (3.100 Å average) in fair agreement with room temperature X-ray crystallographic average values of d_{CH} (2.60 Å) and d_{CC} (3.104 Å), *cf.* Fig. 4. These parameters are significantly larger than the average values measured for the lower homologous aromatic dyotropomers **18** where d_{CH} is 2.43 Å and d_{CC} is 3.070 Å, (which are also in good agreement with the calculated values of 2.40 and 3.09 Å, respectively). Calculated values of ΔH_f, E_s and E_π for triene **30** give ΔE_s (**30** → **31**) 0.38 kcal mol^{-1}, *i.e.*, **31**, like **18**, less strained than its precursor, and ΔE_π (**30** → **31**) ≅ ΔE_π (**17** → **18**). If it is assumed that the necessarily differing trajectories of the transferring H atoms in trienes **17** and **30** have no significant kinetic effect, valid if the argument that many reactions have a rather wide angular 'window' provided the interacting centres are within the van der Waals' distance[4,19] (here *ca.* 2.67 Å), the *ca.* 10^4 rate-ratio for trienes **17**:**30** correlates with a d_{CH} attenuation of 0.1–0.17 Å in **17** compared with **30**. This impressively large rate spread concomitant with a 6–9% modulation in d_{CH} is in excellent agreement with data from thermoneutral dyotropy of compounds **15**.[8a]†

The Effect of Receptor-site Proximate Methylene Bridge Substituents.—Alternative structural modifications might provide further insight into factors controlling the rate of dyotropic rearrangements, particularly the electronic effect of electronegative substituents at the methylene bridge proximate to the receptor π-bond. It is known for example that the π-energy for 7-*anti*-methoxynorbornene is reduced by 0.15–0.24 eV (3.45–5.52 kcal mol^{-1}) compared with norbornene.[22] The chemical consequences of this electronic effect are manifest in several observations relevant to the present work. For example we and

* We thank Brookhaven National Laboratory and Dr. R. K. McMullan for additional facilities relating to neutron diffraction studies.

† It is generally relevant that the vibrational amplitude of a C–H bond is *ca.* 0.1 Å in the lowest vibrational energy level.[20] Allowing for the angular disposition of transferring H atoms, this translated into an attentuation of at least 1.5% (0.04 Å) in d_{CH} for all the dyotropically active trienes discussed here. Certainly internuclear separation is well within the zone where chemical interaction is predicted to become significant.[21]



35 R = $R^{1,2}$ = Cl R^3 = OEt R^4 = H $Ar^{1,2}$ = Ph

	36 $Ar^{1,2}$ = Ph ⟶	**40**
R = R^{1-3} = Cl	**37** $Ar^{1,2}$ = *p*-MeC_6H_4	**41**
R^4 = H	**38** $Ar^{1,2}$ = *p*-ClC_6H_4	**42**
	39 Ar^1 = *p*-MeC_6H_4; Ar^2 = *p*-ClC_6H_4	**43**
	44 R = $R^{2,3}$ = Cl; R^1 = H; $Ar^{1,2}$ = Ph	**47**
R^4 = H	**45** R = $R^{1,3}$ = Cl; R^2 = H; $Ar^{1,2}$ = Ph	**48**
	46 R = R^3 = Cl; $R^{1,2}$ = H; $Ar^{1,2}$ = Ph	**49**
	50 $Ar^{1,2}$ = Ph	**53**
R = R^{1-4} = H	**51** $Ar^{1,2}$ = *p*-MeC_6H_4	**54**
	52 $Ar^{1,2}$ = *p*-ClC_6H_4	**55**
	56 R = R^{1-3} = Cl; R^4 = Bu^{t}O; $Ar^{1,2}$ = *p*-ClC_6H_4	**58**
	57 R = $R^{1,3,4}$ = H; R^2 = Bu^{t}O; $Ar^{1,2}$ = Ph	**59**

Scheme 3

others have observed that the dienophile 12-*anti*-*tert*-butoxyisodrin **1** (R^5 = Bu^{t}O) is inert to TCTD at *ca.* 25 °C (but reacts readily on heating at 110 °C the product losing SO_2 and then undergoing dyotropic aromatisation)[23] in stark contrast with isodrin analogues **19–21** which slowly react with this reagent at ambient temperature (giving trienes **22–24**). However, usefully, dehalogenation of **1** (R^5 = Bu^{t}O) gives **32** (R = Bu^{t}O), which has two potentially dienophilic sites, but reacts rapidly only at the site remote from the Bu^{t}O substituent when contacted with TCTD (as indicated by NMR and *m/z* evidence). Taken with the reduced overall reactivity of this dienophile **32** (RBu^{t}O) compared with **32** (R=H) in an inverse electronic demand cycloaddition, the facts point to HOMO π-energy lowering in the former structure compared with the latter. In simpler terms this may be visualised as arising from inductive electronic withdrawal by the proximate polarised Bu^{t}OCH bridge, and lifting of the degeneracy of the π-energy levels characteristic of **32** (R=H). The effect is very clearly seen from the PES spectra of these two compounds, where the experimentally determined π-energies for **32** (R=H) are $E_{\pi(-)}$ −8.08 eV (HOMO) and $E_{\pi(+)}$ −9.34 (ΔE_π, 1.26 eV).[24] For **32** (R = Bu^{t}O) on the other hand $E_{\pi(-)}$ (HOMO) is indeed at lower energy, −8.60 eV, with $E_{\pi(+)}$ at −8.90 eV and π/π splitting reduced to ΔE_π, 0.3 eV as expected from the loss of π/π degeneracy).*

All these observations are relevant not only to the slower cycloaddition of **32** (R = Bu^{t}O) when contacted with TCTD but more importantly to the retarded dyotropy of the product **33**. At 0.36 mol dm^{-3} conc. in each reactant in $CDCl_3$, triene **33** is seen to form and rearrange with a dyoptropic rate constant k_1 approximating to the bimolecular rate constant for its formation, k_2, 1.45 × 10^{-3} dm^3 mol^{-1} s^{-1} giving a relative dyotropic rate-ratio **17**:**33** ≅ 27. The magnitude of reduction in dyotropic rate for **33** compared with **17** is rather like that observed in the sequence of compounds **23**, **22** and **24** compared with triene **5** where the relative rate spread is 17, and it seems very likely that the rate spread for these compounds does reflect, at least in part, receptor π-energy changes consequent on the presence or otherwise of bridge methylene Cl atoms, and associated polarisation effects. A detailed analysis of the X-ray crystal structure of homoisodrin, comparing C–C and C–Cl bond-lengths and Cl–Cl contact distances, for example, indicates a complex interplay of effects in the halogenated rings of these compounds, the most important of which involves compression between bridgehead Cl atoms and the bridge-methylene Cl atom *syn* to the double bond.[16b] It is therefore likely that partial or complete dehalogenation at this site will also effect the inductive withdrawal by bridgehead Cl atoms proximate to the π-receptor site.

Intramolecular Dyotropy of Pyrazoline Derivatives.—*(I) Kinetic comparison with alicyclic trienes.* In our earlier work[9] we also disclosed kinetic data for irreverisble dyotropy for a series of 1,3-bisarylpyrazolines (Scheme 3) having a reaction-zone cavity expected to be generally similar to that of the trienes depicted in Schemes 1 and 2. All of these compounds except **35** exhibit quantitative irreversible dyotropy† but much less readily than for the alicyclic trienes. For example rate-extrapolation and comparison of di-*p*-tolylpyrazoline **37**, one of the kinetically most active analogues (Tables 4, 5), with the least active triene **24** yields a rate-ratio **24**:**37** of *ca.* 2.3 × 10^2 at 214.9 °C, whilst at this temperature, comparison with the most active reactive (isolable) triene **5** gives a kinetic ratio **5**:**37** of *ca.* 1.7 × 10^3. Kinetic comparison of the bridge-dehalogenated series of diphenylpyrazolines **44**, **45** and **46** with **36** is also invited for comparison with the relative rate-spread (17 at 100 °C) observed for the analogously bridge-dehalogenated trienes **23**, **22** and **24** compared with **5**. Measured values of dyotropic k_1 for the pyrazolines at 214.9 °C yields the relative rate-ratios **36**:**44**:**45**:**46** = 7.3:2.4:1.4:1.0, strongly resembling the computed rate-ratios at this temperature for trienes **5**, **23**, **22** and **24** where relative k_1 values are found to be 7.2:1.8:1.7:1.0. Whilst the rate-spread observed is relatively small, the correspondence in kinetic behaviour accompanying parallel structural changes remote from the reaction-zone cavity for both trienes and pyrazolines is striking, and it may reasonably be inferred have a common origin in receptor π-bond energy changes. Such a view again receives strong support from comparison of *tert*-butoxy bridge-substituted pyrazoline

* We thank Prof. R. Gleiter (Heidelberg, Germany) for PES data for diene **32**.

† For example pyrazoline **36** melts at 218–219 °C, solidifies at higher temperature and remelts at 277–278 °C; the purified product, pyrazole **40**, has m.p. 277–279 °C.

Table 4 Unimolecular rate constants for dyotropy, k_1, pyrazolines[a]

Compound	T/°C	$k_1/10^{-5}$ s^{-1}
36	185.7	3.38
	190.1	4.75
	196.0	7.40
	201.3	10.8
	205.2	13.99
37	185.7	5.28
	191.7	8.39
	196.7	12.3
	202.1	18.7
	207.6	27.9
38	185.7	2.34
	193.0	3.94
	196.7	5.15
	199.5	6.28
	207.6	11.04
39	191.5	7.44
	196.7	11.1
	201.3	15.5
	207.6	24.2
	214.9	40.9
44	196.5	1.89
	207.6	4.47
	214.9	7.85
45	196.5	1.09
	207.6	2.62
	214.9	4.67
46	196.5	0.727
	207.6	1.71
	214.9	3.22
52	165.2	6.65
	170.1	9.72
	177.1	16.2
	185.7	31.1
	190.7	43.2
56	185.7	10.7
	190.5	15.3
	196.7	24.9
	200.1	32.7
	205.2	46.1
	214.9	90.4
57	185.7	21.9
	190.0	30.4
	196.7	49.6
	205.2	86.2
	214.9	167
60	139.9	8.08
	145.1	12.8
	150.0	19.1
	155.5	29.0
	160.0	42.8
	165.5	64.7
61	140.0	5.23
	145.1	8.11
	150.0	12.0
	155.5	19.0
	160.2	28.0
	165.3	41.8

[a] Total number log [comp.]/time data-points collected, 238 (non-correlating data-points neglected, 11). Standard deviations:

$$\frac{\sigma(n-1)}{k_1} \times 100,\ \pm 0.17\text{–}6.8\%,\ \text{average}\ \pm 2.48\%.$$

Data-points collected in random replicate experiments, 58. Average difference in isothermal k_1 values ± 1.11%.

57 with its bridge-unsubstituted analogue **50**;[9] at 165.2 °C the rate-ratio **50**:**57** is computed to be *ca.* 2.0, consistent with a slightly lower exothermicity for dyotropy of *tert*-butoxy compound **57** accompanying some inductive reduction in receptor π-energy. This result also supports the view that the intra-series rate-spread (*ca.* 7) for both trienes **5**, **23**, **22** and **24** and pyrazolines **36**, **44**, **45** and **46** reflects differential receptor π-energies. On the other hand, the inter-series rate comparisons, *e.g.*, of trienes **5** and **24** with pyrazoline **37** suggests that the slower rates of dyotropy observed for the pyrazolines, whilst probably affected by quite small differences in relevant d_{CH} values, mainly reflect the requirements for π-electronic rearrangements in the aromatising alicyclic and heterocyclic 4π-elements. Certainly the remote substituent effects common to both trienes and pyrazolines indicate that the relevant transition-states, whilst of different energy cannot be grossly different in character.

(II) X-Ray crystallographic correlations. Cogently, the X-ray data for bis-*p*-tolylpyrazoline **37** (Table 6) yields d_{CH} values of 2.42 and 2.51 Å, average 2.46 Å, identical with that calculated for triene **5**, and very close to the measured value for triene **24**. OFIT superposition of the lattice frameworks of pyrazoline **37** and its dyotropomer **41** again show virtual spatial coincidence, particularly for the carbon atoms defining the reaction-zone (Fig. 5). In comparison with triene **24** however the sp^2-C receptor sites in the pyrazoline are quite significantly *endo*-pyramidalised, *i.e.*, in the opposite sense to the *exo*-pyramidalisation seen in triene **24**. If, as has been suggested,[10,15] reaction-zone π-density modulates dyotropic rate, pyrazoline **37** will exhibit some rate increase whilst triene **24** will be retarded by this effect. The dyotropic rate-ratio for isoapostatic triene **24** and pyrazoline **37**, 2.3 × 10^2 at 214.9 °C, therefore probably represents a minimum value in terms of the effect on rate by the differing requirements for aromatisation of the two systems.

Further inter-series comparisons between trienes and pyrazolines are also revealing. For instance the average measured d_{CH} for triene **24** is 2.47 Å and identical with that for 7-*p*-chlorophenyl-5-*N*-*p*-tolylpyrazoline **39** (Tables 3 and 6). The rate ratio **24**:**39** is also 2.3 × 10^2 at 214.9 °C, the rate constant, k_1, for pyrazolines **37** and **39**, being almost indistinguishable at this temperature (and also at 196.7 °C, Table 4). Similarly for triene **7** and pyrazoline **37** with identical average d_{CH} values, the rate-ratio **7**:**37** is 2.4 × 10^2, whilst comparison of isoapostatic triene **5** with pyrazoline **37** yields a rate-ratio **5**:**37** of 1.7 × 10^3. The rate ratio of 10^{-2}–10^{-3} for the kinetically retarded pyrazolines in comparison with the alicyclic trienes is, then, most reasonably identified as arising from factors other than the reaction-zone cavity parameter, d_{CH}, and subsumes the effect of differing sp^2-C pyramidalisation at the receptor π-bonds and the stereoelectronic requirements for rehybridisation/aromatisation at the H-donor sites in the two series of compounds.*

The very close similarity in dyotropic rates for pyrazolines **37** and **39** with almost isoapostatic d_{CH} (Δd_{CH} **37**, **39** = 0.01 Å) reveals, as expected for a process having a reactant-like transition state, the relatively small kinetic effect of differing aryl substituents in the 2 H donor pyrazoline rings, and the consistency of reaction-zone cavity parameters and rate-data is striking.

Dyotropy of Pyrazolines Derived from Homoisodrin, **28**, *and Comparison with Isodrin-derived Lower Homologues.*—Further information for structure–reactivity correlations is obtained by the kinetic/structural study of bisarylpyrazolines obtained

* The available X-ray and neutron diffraction data indicate relatively small differences between trienes and pyrazolines with respect to the angular disposition of transferring H atoms, as defined, respectively, by H(4)–C(4)–C(9), H(9)–C(9)–C(4) and by H(4)–C(4)–C(8), H(8)–C(8)–C(4). The difference in the average angle between the two series of compounds is 2.5–7.5 ± 2°, of the same order of magnitude as found for kinetically similar pyrazolines **37** and **39**, which differ in this respect by 5.2–6.7 ± 2°.

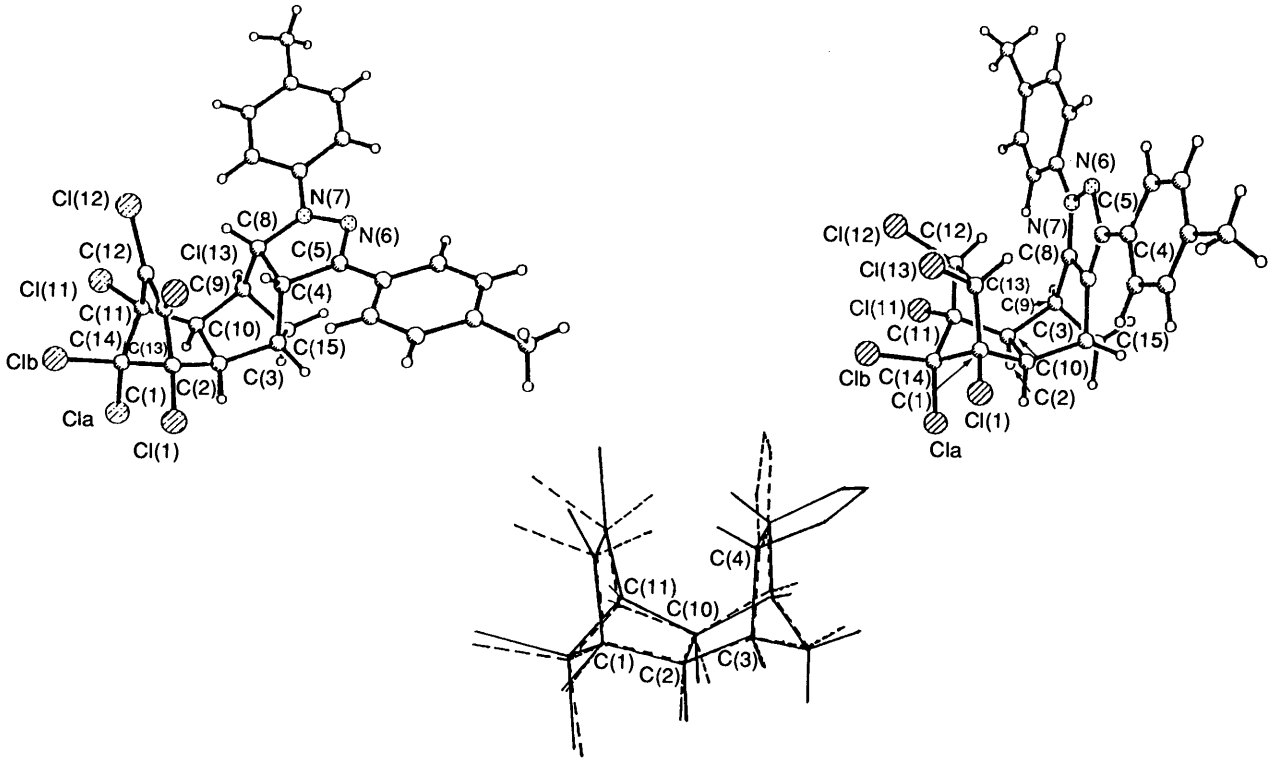


Fig. 5 Computer-generated perspective representations of pyrazoline **37** and its dyotropomer **41** with OFIT super-position (aryl rings omitted for clarity)

Table 5 Activation parameters for dyotropy-pyrazolines

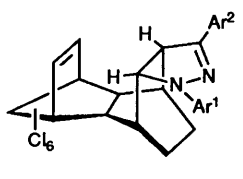
Compound	E_a [a]	$\Delta H^{\ddagger}$ [a]	$\Delta S^{\ddagger}$ [b]	$\Delta G^{\ddagger}$ [a]	log A
36	31.88 ± 0.27	31.29 ± 0.26	−11.55 ± 0.14	34.73	10.7 ± 0.13
37	33.44 ± 0.16	32.85 ± 0.16	−7.29 ± 0.05	35.02	11.63 ± 0.08
38	31.11 ± 0.17	30.52 ± 0.16	−14.00 ± 0.11	34.69	10.17 ± 0.08
39	32.72 ± 0.16	32.13 ± 0.16	−9.06 ± 0.06	34.83	11.25 ± 0.08
52	29.81 ± 0.24	29.22 ± 0.23	−11.69 ± 0.13	32.71	10.67 ± 0.12
56	32.69 ± 0.30	32.09 ± 0.29(6)	−7.52 ± 0.09	34.33(7)	11.58 ± 0.14
57	30.77 ± 0.27	30.18 ± 0.27	−10.25 ± 0.12	33.24	10.99 ± 0.13
60	29.29 ± 0.16	28.69 ± 0.16	−8.39(9) ± 0.06	31.19(8)	11.39 ± 0.08
61	29.60 ± 0.17	29.01 ± 0.16	−8.54 ± 0.06	31.56	11.36 ± 0.09

[a] kcal mol^{-1}. [b] cal mol^{-1} K^{-1} converted from data expressed in kJ and J.

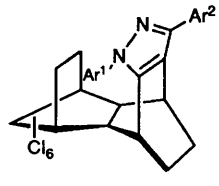
Table 6 Internuclear distances, d_{CC} and d_{CH}, pyrazolines and pyrazoles (X-ray data)

Compound	d_{CC}/Å	d_{CH}/Å	Compound	d_{CC}	d_{CH}
37	3.024	2.420	**41**	3.037	2.327
	3.023	2.511		3.023	2.222
39	3.023	2.452	**43**	—	—
	3.018	2.459			
60	3.054	2.54	**62**	3.004	2.27
	3.050	2.46		3.004	2.27
61			**63**	2.938	2.200
				3.050	2.282

from homoisodrin **28** and its parent hydrocarbon, **29**. Here the usual method of synthesis of the required diphenyl- and bis(*p*-chlorophenyl)-pyrazolines **60** and **61** by capture of relevant 1,3-diarylnitrilimines released by thermolysis of appropriate 2,5-bisaryltetrazoles, delivers instead their respective rearrangement products, dyotropomers **62** and **63**, the first indication of accelerated dyotropy for these compounds compared with the isodrin-derived, lower homologues, **36**, **38**. Small but useful quantities of the required pyrazolines **60** and **61** can be obtained, however, by brief thermolysis of an intimate mixture of dipolarophile **28** with a large (four-fold) excess of the relevant tetrazole, followed by product separation from largely unchanged materials. Dyotropic rate data and activation parameters for pyrazolines **60** and **61** are included in Tables 4 and 5. It is instructive to compare the relative dyotropic rates of **60** and **61** with those of the lower homologues **36** and **38**, which have the same pyrazoline arylation pattern. The relative rate-ratio **60**:**61** is 1.54 at 214.9 °C, essentially the same as this ratio for **36**:**38** = 1.53 at the same temperature, an unambiguous indication of the identical and small magnitude of aryl-



60 $Ar^{1,2}$ = Ph
61 $Ar^{1,2}$ = *p*-ClC_6H_4



62
63

Table 7 Unimolecular rate constants for dyotropy, ^{1}H- and ^{2}H-trienes **5** and -pyrazolines **38**

Compound	T/°C	$k_1/10^{-5}$ s^{-1}
[^{1}H]-**5**[a]	75	2.34
	79.8	3.85
	82.2	4.85
	84.8	6.26
	87.7	8.46
	90.0	10.6
	95.0	16.6
	96.0	18.4
	99.9	26.2
[^{2}H]-**5**[b]	98.7	3.03
	104.1	5.08
	108.7	7.73
	110.7	9.41(7)
	114.1	12.6
	115.7	14.8
	118.9	19.5
	123.8	29.9
[^{2}H]-**38**[c]	183.1	1.87
	185.7	2.34
	190.0	3.14
	193.0	3.94
	196.7	5.15
	199.5	6.28
	207.6	11.04
[^{2}H]-**38**[d]	195.1	0.965
	199.9	1.34
	205.0	2.05
	207.6	2.39(8)
	215.0	4.26
	217.0	4.92
	220.0	6.02
	224.9	8.54

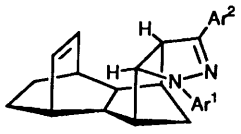
Total number log [comp.]/time data-points collected, (non-correlating data-points neglected), standard deviations,

$$\left(\frac{\sigma(n-1)}{k_1}\right) \times 100$$

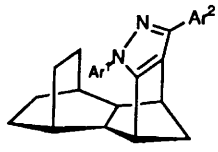
range %, average %: [a] 50, (0), ±0.5–2.47%, ±1.38%. [b] 40, (2), ±0.33–3.16%, ±1.78%. [c] 33, (2), ±0.66–4.98%, ±2.29%. [d] 37, (0), ±1.41–4.53%, ±2.73%.

substituent effects in the two series of pyrazolines. If across-series comparisons are made, *viz.* **60**, with the identically substituted isodrin derivative **36**, and likewise between **61** and its lower homologue **38**, the rate-ratios are nearly identical, **60**:**36** = 75 and **61**:**38** = 72. This result indicates a constant accelerating factor in the homoisodrin derivatives compared with the lower homologous isodrin compounds. Since the rate differential of nearly 10^2 between the two series of compounds could arise from, *e.g.*, differing d_{CH} values, structural information is invited.

X-Ray structural parameters for pyrazoline **60** (Table 6) give d_{CH} = 2.54 and 2.46 Å (2.50 Å average) whilst its dyotropomer **62** has d_{CH} = 2.27 Å, this molecule being unusually symmetrical. For comparison dyotropomer **63** of (unfortunately) X-ray unstable pyrazoline **61** has d_{CH} 2.20 and 2.28 Å (2.24 Å average). If rates of dyotropy are compared for homoisodrin and isodrin derived structures where d_{CH} values are experimentally known, *e.g.*, diphenylpyrazoline **60** with d_{CH} 2.54 and 2.46 Å (2.50 Å average) and bis-*p*-tolylpyrazoline **37** with d_{CH} 2.42 and 2.51 Å (2.46 Å average) a relative rate-ratio **60**:**37** of 42.5 is observed (214.9 °C), *ca.* 25 times larger than expected from the differing pyrazoline substitution pattern, given the close similarity of aryl-substituent effects in the two homologous series, and that the rate-ratio for diphenyl- and bis-*p*-tolylpyrazolines **36** and **37** is merely 1.7 at the same temperature. (The measured d_{CH} values averaged for pyrazolines **37** and **39** is also 2.46 Å and very close to the actual values for each molecular structure). On this basis of comparison, the d_{CH} value for pyrazoline **60** is significantly larger (2.50 Å) than the characteristic value of d_{CH} in the lower homologous isodrin derived series, and here we see the first instance where a slight amplification in the relevant d_{CH} parameter is associated with accelerated dyotropy for a molecule having otherwise similar electronic requirements in the rearrangement process. In comparing pyrazolines **60** and **61** with the lower homologues **36**, **37** and **38**, the possibility of steric acceleration consequent on the introduction of an additional CH_2 group proximate to the pyrazoline ring and its aryl substituents, raising the ground state energy slightly relative to **36**–**38**, seems the most likely rationale. Cogently relevant in this connection is the recent observation that when d_{CH} values remain isoapostatic, ground-state steric effects can translate into quite large kinetic effects in cases of thermoneutral dyotropy,[8b] with an observed rate-spread of *ca.* 10^4 among a series of related compounds. As expected then, the steric effect of the additional CH_2 group is small, but significant.



64 $Ar^{1,2}$ = *p*-ClC_6H_4



65

A contrasting and at first sight surprising result is seen in the slower dyotropy for the dehalogenated pyrazoline **64** compared with the lower homologue **52**,[9] with a relative rate-ratio **52**: **64** ~ 16 at 156 °C. In the regiochemically different situation where the receptor π-bond forms part of a bicyclo[2.2.1]heptene system, *e.g.*, in compounds **61** and **38** as opposed to a bicyclo[2.2.2]octene element (as in **64**), but where the pyrazoline ring substituents are the same, the rate differential is much larger, with a relative rate ratio **61**:**38** ~ 10^2 at 156 °C. The relatively slow dyotropy of pyrazoline **64** may however best be accounted for by the expected amplification of d_{CH}, in the absence of steric acceleration associated with an ethano bridge proximate to the donor pyrazoline ring.

Primary Deuterium Kinetic Isotope Effects (*PDKIE*).—From the X-ray and neutron scattering crystallographic data presented here, it has been rigorously determined that d_{CH} in molecules analogous to triene **5** and pyrazoline **36** is within the van der Waals' radius (*ca.* 2.67 Å) at a distance predicted by theory[21] appropriate to the onset of chemical interaction. The reacting centres are not however ideally colinear as assumed in theoretical models for intermolecular dyotropy.[6b] Theory suggests that non-linear and thermochemically unsymmetrical transition-states for H-transfer reactions correlate with an attentuated PDKIE.[6c] For this and other reasons it seemed to us of interest to prepare hexadeuterio analogues of triene **5** and pyrazoline **38**, as representative examples, to investigate the magnitude of the respective isotopic-isomer rate-ratios k_1^{2H}/k_1^{2D}. Such experiments are also invited for their potential in distinguishing synchronous from two-stage processes during 2 H-transfer.[6b,d] In addition, especially for the pyrazolines, the proximity of the interacting centres, with an estimated H-nucleus displacement of *ca.* 1.7 Å in the H-transfer step determined from the crystallographic data and a likely narrow but relatively high activation barrier, raises the possibility of a significant quantum tunnelling contribution to the rearrange-

ment kinetics.[25a,c,d] It is also important to know generally whether a quantum tunnelling contribution might be in part responsible for the accelerated reaction-rates often observed for intramolecular processes,[3] and the molecules we have described here which display intramolecular dyotropy make excellent models for probing such effects.

The required deuterium-labelled analogues of triene **5** and pyrazoline **38** were made using the following strategy. Freshly cracked cyclopentadiene was heated with an excess of 99.98% isotopically pure NaOD–D_2O mixtures, and the diene allowed spontaneously to convert into the prototropically unreative dimer (to facilitate handling). ^{1}H NMR and mass-spectrometry indicated 70% random incorporation of ^{2}H (≡D) in the dicyclopentadiene product. Thermolysis of this product and immediate use of the monomer in (pressure-tube) cycloaddition with 1,2,3,4,7,7-hexachloronorborna-2,5-diene gives isodrin **1** 70% randomly ^{2}H-labelled at bridgehead (C-1,8), etheno (C-9,10) and bridge-methylene (C-12) positions, with 100% ^{1}H at the ring-junction sites, C-2, -7 (^{1}H NMR 400 MHz). ^{2}H-Labelled triene **5** and pyrazoline **38** were then prepared from ^{2}H-**1** as previously described.[9] Preliminary kinetic experiments with 70% ^{2}H-**5** and 70% ^{2}H-**38** showed the expected behaviour for mixed isotopic species, an initially curved log (composition)/t plot finally becoming linear after several half-lives appropriate to the protio compounds at the relevant temperature (95 °C and 207.6 °C, respectively for triene **5** and pyrazoline **38**). Each compound exhibited a considerable PDKIE, advantageously translated into the almost quantitative selective removal[25b] of ^{1}H from C-4,9 in triene **5** and from C-4,8 in pyrazoline **38**, by heating decalin solutions of 70% ^{2}H-**5** and 70% ^{2}H-**38** for eight half-lives with respect to the ^{1}H compounds at the above temperatures, employing the kinetic data of Tables 1 and 4 (above). Preparative TLC separation of unchanged triene **5** from the thermolysis product gave pure compound with 98.8% ^{2}H at each of C-4,9 (^{1}H NMR 400 MHz) and a similar recovery and analysis of unchanged pyrazoline **38** delivered a product with >98% ^{2}H at C-4,8. Depletion of 4,9-^{1}H-**5** and 4,8-^{1}H-**38** was seen to be rather close to that predicted by their kinetic parameters (99.6%), indicating a negligible β secondary DKIE as expected[25a] from the structural features, with torsion angles H-3/4, H-9,10 (**5**) and H-3/4, H-8,9 (**38**) *ca.* 90°.

Heating solutions of ^{2}H-**5** and ^{2}H-**38** over a range of temperatures and times as for ^{1}H analogues gave the kinetic data in Table 7, which may be compared with additional data for the ^{1}H isotopic isomers, necessarily required to widen the temperature range in each case for more exact comparison. The kinetic data for ^{1}H-**5**, ^{2}H-**5** and ^{1}H-**38**, ^{2}H-**38** gave excellent ln k_1/K^{-1} Arrhenius plots and linear regression analysis computation gave the thermochemical parameters presented in Table 8.

For trienes **5** a mean PDKIE ratio k_1^{2H}/k_1^{2D} of 7.74 is calculated at 100 °C,* whilst for the pyrazolines **38** direct comparison at 207.6 °C yields $k_1^{2H}/k_2^{2D} = 4.60 \pm 0.29$. For comparison with k_1^{2H}/k_1^{2D} for trienes **5**, this ratio, extrapolated to 100 °C, increases to 10.8. Rate extrapolation to 25 °C using the data of Table 8 yields for the trienes **5** $k_1^{2H}/k_1^{2D} = 13.8$ and for pyrazolines **38**, $k_1^{2H}/k_1^{2D} = 28.2$ a reflection of the PDKIE temperature dependence. The temperature dependence, the slope for $\ln[k_1^{2H}/k_1^{2D}]$ *vs.* K^{-1}, is 0.859 for trienes **5** and strikingly, much larger—1.420—for the pyrazolines **38**. However the most revealing difference in the data for the isotopic isomer-pairs of **5** and **38** lies in the values of the Arrehenius pre-exponential a factor ratios, A_{2H}/A_{2D} which are 0.800 ± 0.200 and 0.284 ± 0.143, respectively (Table 8).) Values of this ratio of ≤0.80 ± 0.10 and a steep temperature dependence for the PDKIE are usually regarded as a reliable indication of a quantum tunnelling contribution.[25a,d] For the pyrazolines **38** the magnitude of the PDKIE, steep temperature dependence and fractional value of A_{2H}/A_{2D} (which is similar to values reported in a number of reactions where quantum tunnelling is reasonably well established)[25a] together with $\Delta E_a^{2D} - \Delta E_a^{2H} = 2.80 \pm 0.51$ kcal mol^{-1}, the mean value being in excess of the ground state C-2H/C-2D zero-point vibrational energy difference (2 × 1.20 kcal mol^{-1}), strongly suggest non-classical behaviour. For treiene **5** the situation is less clear-cut; although the size of the PDKIE at 25 °C may be an indication of a tunnelling contribution, $\Delta E_a^{2D} - \Delta E_a^{2H} = 1.7 \pm 0.22$ kcal mol^{-1}, less than the zero-point-energy difference for C-2H/C-2D. However the data for the trienes **5** may be usefully compared, with due caution, with theoretical calculations for the similarly exothermic diimide–ethene reaction by intermolecular 2 H transfer;[6b] these indicate a significantly larger computed PDKIE k_1^{2H}/k_1^{2D} of *ca.* 11.8 at 25 °C for a synchronous pericyclic process than for a stepwise reaction, which is calculated to have k_1^{2H}/k_1^{2D} ~9 at this temperature. The magnitude of k_1^{2H}/k_1^{2D}, extrapolated to 25 °C for trienes **5**, at 13.8, perhaps suggests a synchronous process, and this might seem likely from the proximity of the interacting centres provided it can be reasonably assumed that asymmetric 'in–out' skeletal vibrations of the relatively massive halogenated carbon framework which define the reaction zone are not coupled to the 2 H-transfer process. Clearly however more work is needed to clarify this point.†

For a reaction having a thermochemically unsymmetrical transition state, the relevant C–H(D) vibrations may not entirely vanish in the transition-state.[26] The difference in activation energy for the two isotopic species $E_a^{2H} - E_a^{2D}$ may then not simply be the difference in ground-state C–H/C–D zero-point vibrational energy (1.2 kcal per D atom). If the increment to activation energy resulting from isotopic substitution is represented by $\delta E_a(\nu_o)$ then $\Delta E_a^{2D} = \Delta E_a^{2H} + \delta E_a(\nu_o)$. Inspection of a diagrammatic reaction coordinate taking into account ground-state and transition-state vibrational energy differences[25a,26] shows that $\Delta E_a^{2D} = \Delta E_a^{2H} + \delta E_a(\nu_o)_{gs} - \delta E_a(\nu_o)_{ts}$. Evaluation of $\delta E_a(\nu_o)$ from the slope of ln (k_1^{2H}/k_1^{2D}) *vs.* K^{-1} gives values of 0.852 kcal mol^{-1} per D atom for triene **5**, and 1.4 kcal mol^{-1} per D for the pyrazolines **38** (in agreement with figures obtained from $\Delta H^{\ddagger 2D} - \Delta H^{\ddagger 2H}$ in each case).[25a] Since $\delta E_a(\nu_o) = \delta E_a(\nu_o)_{gs} - \delta E_a(\nu_o)_{ts}$ and $\delta E_a(\nu_o)_{gs}$ is known to be 1.20 kcal mol^{-1} for C–H/C–D,[25a] for

* For comparison with the PDKIE evaluated at 160.7 °C for the 4*n* homologous dyotropy reported by Grimme *et al.*[6d] ($k_1^{2H}/k_1^{2D} = 3.16$), for trienes **5** k_1^{2H}/k_1^{2D} is calculable to be 5.6 at this temperature.

† For the isoapostatic trienes and pyrazolines **5** and **37**; **24** and **37**; **24** and **39**; **7** and **37**, the measured $\Delta H^{\ddagger}$ values for the pyrazolines are from 4.4–8.4 kcal mol^{-1} larger than for the trienes. If measured values of $\Delta H^{\ddagger}$ (and E_a) in reality correspond to the energies of biradical intermediates produced in a rate-limiting, barrier-avoiding tunnelling transfer of one H$^{\bullet}$,[8c] the bis-arylated pyrazolines would be expected to deliver the more stable, lower-energy intermediate, the opposite of what is found here. In addition, the hexahalogenated pyrazoline **38** has larger E_a and $\Delta H^{\ddagger}$ than the dehalogenated analogue **52**, contrary to expectation based on stabilised intermediates being involved. Moreover, on the basis of the exothermicity (ΔE) observed in the dyotropy of triene **24** (−22.6 kcal mol^{-1}), the calculated $E_{a,0}$ for an equivalent thermoneutral process, derived from[26] $E_a = E_{a,0}(1 + \Delta E/4E_{a,0})$,[2] is 39.6 kcal mol^{-1}. This is rather close to the estimated value of E_a for thermoneutral dyotropy of the furan derivative **13** (35–39 kcal mol^{-1}) and to E_a calculated for the relatively thermoneutral dyotropy of isoapostatic compound **15** (R = H_2), 36.5 kcal mol^{-1}, calculated from data provided.[8a] It would be quite remarkable that such a favourable correlation exists between $E_{a,0}$ for thermoneutral dyotropy of **13** and **15** and E_a for the exothermic reaction of triene **24**, given their very different composition and structure, if their rearrangements involved biradical intermediates.

Table 8 Activation parameters for dyotropy, ^{1}H- and ^{2}H-trienes **5** and -pyrazolines **38**

	ΔE_a[a]	$\Delta H^{\ddagger}$[a]	$\Delta S^{\ddagger}$[b]	$\Delta G^{\ddagger}$[a]	log A
[^{1}H]-**5**	25.07 ± 0.07	24.47 ± 0.09	−9.87 ± 0.05	27.39	11.09 ± 0.06
[^{2}H]-**5**[c]	26.77 ± 0.09	26.18 ± 0.09	−9.27 ± 0.04(5)	28.95	11.20 ± 0.05
[^{1}H]-**38**	31.43 ± 0.21	30.83 ± 0.20	−13.33 ± 0.12	34.81	10.32 ± 0.10
[^{2}H]-**38**[c]	34.23 ± 0.30	33.63 ± 0.29(6)	−10.49 ± 0.13	36.76	10.93 ± 0.14

[a] kcal mol^{-1}. [b] cals mol^{-1} K^{-1} converted from data in kJ, (1 cal = 4.18 J). [c] To simplify expressions used in describing and discussing data ^{2}H ≡ D.

the trienes **5** the apparent value of $\delta E_a(\nu_o)_{ts}$ is then +0.35 kcal mol^{-1} per D atom, but for the pyrazolines this term has a negative value, −0.20 kcal mol^{-1} per D atom, perhaps also an indication of non-classical behaviour in the pyrazolines **38**.

In future work we intend computer analysis of the PDKIE data described here (and others in course of acquisition) using a program enabling experimental data to be fitted[25a,d] to the Bell equation[25c] relating the tunnelling frequency to tunnelling correction coefficients Q_t^H, Q_t^D. It may then be possible to obtain a value for the activation barrier half-width 'a' for comparison with X-ray (and neutron) crystallographic parameters for ^{2}H-**38** and ^{2}H-**5**. This is an important objective since most information about tunnelling effects relates to intermolecular reactions for which barrier parameters, *e.g.*, distance traverse for transferring H atoms, cannot be so directly correlated with experimental structural data. There is also relatively little experimental information about barrier parameters,[27] certainly none to our knowledge for instances of intramolecular dyotropy other than measured, comparable, values of ΔE_a.[6d,9]

Experimental

The following apply unless otherwise indicated. NMR data refer to solutions in $CDCl_3$ (Me_4Si), obtained using JEOL GX270, GX400 or GSX500 instruments; all signals have the correct relative intensities. UV spectroscopic data required for kinetic monitoring were obtained for solutions in EtOH or decalin using PE 555 and 552 instruments. EI mass spectra were obtained with probe samples using an AEI MS902 machine with VG Micromass facilities; all ion-clusters have the correct characteristic halogen-isotope abundance ratios in appropriate cases. Preparative TLC refers to 0.8 mm Merck Type 60 GF_{254} silica gel coated plates visualised under UV light. Light petroleum refers to the 60–80 °C b.p. fraction. Kinetic data are for solutions in decalin; air-sensitive pyrazoline solutions were air-purged by freeze–thaw (−196 °C) cycles under N_2 and then vacuum several times before ampoules were sealed *in vacuo*. Ampoules were heated in a Grant thermostat fitted with a calibrated thermometer, (±0.1 °C); temperatures cited represent the estimated mean values over runs, solutions being monitored and corrected for background absorption at the principal UV λ_{max} using PE 555 or 552 digital display spectrometers. Kinetic runs were conducted in most experiments over time intervals of 1.0–3.0 half-lives, it having been found that rearrangements proceeded unimolecularly virtually to completion on prolonged heating. Random duplicate runs in preliminary and later (PDKIE) experiments consistently indicated reproducibility of k_1 values to within 2%. Arrhenius plots had residual factors (R^2) of better than 0.998 in every case. X-Ray crystal structures were obtained using a Siemens R3m/V diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.710 69 Å). Tables of fractional coordinates, bond lengths, bond angles and other data have been deposited at the Cambridge Crystallographic Data Centre.*

* For details of the CCDC deposition scheme, see 'Instructions for Authors (1993)', *J. Chem. Soc., Perkin Trans. 2*, 1993, issue 1.

Synthesis and Characterisation of Alicyclic Trienes, and their Dyotropomers.—Crystallographically suitable single crystals of dechloroethoxyisodrin **3**, the derived triene **7** and dyotropomer **11** were obtained from original samples.[5a]

Crystal data. **3**, $C_{14}H_{13}Cl_5O$, M = 374.5, a = 8.057(3), b = 11.803(5), c = 16.911(6) Å, β = 101.050(0)°. Space group $P2_1/c$, U = 1578.4(11) Å^3, Z = 4, D_c 1.576 g cm^{-3}, μ(Mo-Kα) = 9.16 cm^{-1}, F(000) = 760, $R(R')$ 0.039 (0.0546), 2782 data.

7, $C_{18}H_{13}Cl_9O$, M = 564.3, a = 13.669(4), b = 9.348(3), c = 17.089(5) Å, β = 91.790(0)°. Space group $P2_1/c$, U = 2182.3(11) Å^3, Z = 4, D_c = 1.718 g cm^{-3}, F(000) = 1128, $R(R')$ 0.0478 (0.0580), 2495 data. Single crystals of dyotropomer **18**[9a] were similarly obtained.

Crystal data. **18**, $C_{16}H_{14}Cl_4$, M = 348.1, a = 14.731(6), b = 12.492(5), c = 16.463(6) Å, β = 100.280°. Space group $P2_1/c$, U = 2981(2) Å^3, Z = 8, D_c = 1.551 g cm^{-3}, F(000) = 1424 $R(R')$ = 0.0440 (0.0497), 2265 data.

Nona- and Octa-chlorotrienes **22**, **23**, **24**.—11-*syn*-, 11-*anti*- and 11,11-bisdechloroisodrin were obtained by Zu–Cu reduction of isodrin (**1**) in boiling moist ether (**19** and **20**) or by heating with Zu–HOAc (**20**, **21**)[28] and the mixed products separated by TLC. ^{1}H NMR monitoring (10 days) of solutions of **19**, **20**, **21** (0.5 mmol) in contact with tetrachlorothiophene dioxide (TCTD) (0.52 mmol) in $CHCl_3$ (1.5–2 cm^3) at 25 °C indicated slow formation of trienes **22**, **23**, **24** (and faster addition with **19** and **21**). Similar solutions were therefore heated under reflux 72 h, partial evaporation giving respectively, **22**, **23** and **24**[1] (accompanied by their respective dyotropomers **25**, **26** and **27**).

Isolated by recrystallisation: *triene* **22** (97 mg, 37%) endo,-endo,exo-1,5,6,7,8,12,13,14-anti-15-*nonachloropentacyclo*[10.-2.1.1^{3,10}.0.^{2,11}.0^{4,9}]*hexadeca*-5,7,13-*triene*, m.p. 304–305 °C (turning opaque 160–170 °C, rearrangement and crystal disorder, *cf.* **25**). δ 1.72, 1.76 (each quintet, ^2J = 10.8 Hz, H-16*s*), 2.02, 2.06 (each q, ^2J = 10.8 Hz, H-16*a*), 2.97 (sextet, H-3,10), 3.17 (d, J = 1.83 Hz, H-2,11), 3.24 (apparent t, H-4,9) and 4.25 [d, ^6J = 0.9 Hz, H-15*s* (coupled to H-16s)]; λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) 264 (2606), 274 (3966), 285 (5724) 297 (6235) and 311 (3690); m/z 516 (M$^+$), 481 (M$^+$ − Cl), 252 (RDA, $C_9H_4{}^{35}Cl_3{}^{37}Cl$ = 100%) (Found: C, 37.1; H, 1.95. $C_{16}H_9Cl_9$ requires C, 36.93, H, 1.74%).

Isomeric *triene* **23** (*ca.* 40%), m.p. 348–349 °C (turning opaque 150–170 °C, *cf.* **22**); instantaneous melting 240 °C, solidifying and re-melting 348–349 °C.[5b] δ 1.60, 1.65 (each m, ^2J = 11.0 Hz, H-16s), 2.04, 2.08 (d and t, ^2J = 11.0, J ~ 1.6 Hz, H-16a), 3.06 (quintet, H-3,10), 3.18 (d, J = 1.8 Hz, H-2,11), 3.93 (quintet, H-4,9) and 4.46 (sharp s, *cf.* **22**, H-15a); λ_{max}/nm (ε/dm^3, mol^{-1} cm^{-1}) 266 (3122), 275 (3469), 287 (4683), 299 (5203) and 313 (3078); m/z 516 (M$^+$), 481 (M$^+$ − Cl), 252 (RDA 254 = 100%) (Found: C, 37.25; H, 1.85%).

Octachlorotriene **24** (*ca.* 45%), m.p. 188–190 °C, resolidifying and re-melting 242–243 °C (*cf.* **27**). δ 1.68, 1.71 (each quintet, ^2J = 10.8 Hz, H-16s), 2.01, 2.05 (each narrow m, ^2J = 10.8 Hz, H-16a), 2.78 (AB type system, q, H-15,15), 2.95 (sextet, H-3,10) and 3.19 (apparent t, H-2,11 and H-4,9); λ_{max}/nm (ε_{max}/cm^3 mol^{-1} cm^{-1}) 264 (3436), 274 (4705), 285 (6204), 297 (6347) and

311 (3684); *m/z* 482 (M^+), 447 (M^+ − Cl), 252 (RDA 254 = 100%) (Found: C, 39.8; H, 2.3. $C_{16}H_{10}Cl_8$ requires C, 39.55; H, 2.07%).

Crystal data. **22**,[1] $C_{16}H_9Cl_9$, M = 520.3, a = 13.779(6), b = 8.220(3), c = 16.889(7) Å, β = 93.00(3)°. Space group $P2_1/c$ (No. 14), U = 1910(1) Å^3, Z = 4, D_c = 1.82 g cm^{-3}, $F(000)$ = 1032 μ(Mo-Kα) = 13.3 cm^{-1}.

24,[1] $C_{16}H_{10}Cl_8$, M = 485.9, a = 30.842(1), b = 8.588(5), c = 14.296(6) Å, β = 97.17°. Space group $C2/c$ (No. 15), U = 3757 Å^3, Z = 8, D_c = 1.72 g cm^{-3} $F(000)$ = 1936, μ(Mo-Kα) = 12.2 cm^{-1}.

Mo-Kα X-radiation (graphite monochromator) λ = 0.710 73 Å. **22** R (R') 0.0028 (0.031), 1337 data; **24** R (R') 0.044 (0.044), 1597 data.

Neutron diffraction data. **24**, cell constants (15 K) a = 30.450(1), b = 8.4599(4), c = 14.1661(1) Å, β = 97.023(3)°, U = 3622 Å^3, radiation λ = 1.27 Å, μ = 1.56 cm^{-1}, R (R') 0.045 (0.046), 2739 data. R_m all data, 0.01.

No exactly similar structures have been reported, but for two compounds containing the isodrin (**1**) skeletal element, *i.e.*, **32** R = $OCOC_6H_4CO_2H$ d_{CC} = 2.921 Å,[29] whilst for isodrin d_{CC} = 2.87 Å,[30] and for homoisodrin d_{CC} = 2.94 Å[16b] and for the bis-benzo annellated analogue of hexadechloro-**1**, d_{CC} is. 3.04 Å.[31] For dechloroethoxyisodrin **3** we find d_{CC} = 2.89 Å.

Dyotropic Isomers **25**, **26**, **27**.—The recrystallisation residues from the preparation of adduct **22** were further crystallised and the product heated in toluene (110 °C) overnight. The toluene was then evaporated off and the solid recrystallised ($CHCl_3$–light petroleum) to give the *dyotropomer* **25**, endo,endo-1,5,6,7,8,12,13,14-anti-15-*nonachloropentacyclo*[10.2.1.1^{3,10}.0^{2,11}.0^{4,9}]*hexadeca*-4(9),5,7-*triene* (*ca.* 25 mg, 10%), m.p. 304–305 °C. δ 2.04, 2.08 (each t, ^2J = 9.71 Hz, H-16*a*), 2.23, 2.26 (each q, ^2J = 9.71 Hz, ^6J coupling to H-15*s*, H-16*s*), 3.74 (t, ^2J ~ 2, deshielded by Cl-15, H-2,11), 3.85 (quintet, H-3,10), 3.72 (s, H-13,14) and 4.68 (d, ^6J = 0.9 Hz, *cf.* **22**); λ_{max} no absorption near 300 nm; *m/z* 516 (M^+, 520, 34%), 481 (M^+ − Cl) and 252 (RDA, 254, 100%) (Found: C, 37.1; H, 1.8. $C_{16}H_9Cl_9$ requires C, 36.93; H, 1.74%).

Crystal data. **25**, $C_{16}H_9Cl_9$, M = 520.3, a = 8.664(2), b = 8.814(2), c = 14.254(3) Å, α = 89.81(3)°, β = 84.10(3)°, γ = 61.11(3)°. Space group $P\bar{1}$, U = 946.6(4) Å^3, Z = 2, D_c = 1.825 g cm^{-3}, $F(000)$ = 516, μ(Mo-Kα) = 13.4 cm^{-1}, R (R') 0.0335 (0.0397), 3852 data.

Similarly obtained, *dyotropomer* **26** (22 mg, 8.5%), m.p. 347–350 °C (decomp.).[5b] δ 1.87, 1.91 (each t, ^2J = 9.7, ^3J = 1.3 Hz, H-16*a*), 2.19, 2.23 (each *t*, ^2J = 9.7, ^3J ~ 1.7 Hz, H-16*s*), 3.37 (t ^3J ~ 2 Hz, H-2,11), 3.64 (d, ^4J = 1.46 Hz, H-13,14), 3.92 (quintet, H-3,10) and 4.22 (t, ^4J = 1.46 Hz, H-15*a*); λ_{max} no absorption near 300 nm; *m/z* 516 (M^+, 520, 34%), 481 (M^+ − Cl) and 252 (RDA, 254, 100%) (Found: C, 37.12; H, 1.81%).

Crystals of *dyotropomer* **27** were obtained by heating triene **24** (50 mg) in toluene (110 °C) overnight, evaporation and recrystallisation of the solid product from CH_2Cl_2–light petroleum (×2), to give 1,5,6,7,8,12,13,14-*octachloro-pentacyclo*[10.2.1.1^{3,10}.0^{2,11}.0^{4,9}]*hexadeca*-4(9),5,7-*triene* **27** (25 mg, 50%), m.p. 243–244 °C. δ 1.98, 2.01 (each t, ^2J = 9.5 Hz, H-16*a*), 2.20, 2.23 (each q, ^2J = 9.5 Hz, H-16*s*), 2.36, 2.40 (each t, ^2J = 10.3, ^4J = 2.2 Hz, H-15*a*), 2.87, 2.91 [each d, ^2J = 10.3, ^6J = 1.1 Hz (long-range coupling to H-16*s* and deshielded by Cl-13,14, *cf.* **24**), H-15*s*], 3.56–3.59 (m, overlapping H-2,11 and H-13,14) and 3.83 (quintet, H-3,10. UV—no absorption near 300 nm: *m/z* 482 (M^+, 486. $C_{16}H_{10}{}^{35}Cl_6{}^{37}Cl_2$ 29%), 447 (M^+ − Cl), 252 (RDA$^+$, 254 100%) (Found: C, 39.76; H, 2.21. $C_{16}H_{10}Cl_{18}$ requires C, 39.55; H, 2.07%).

Crystal data. **27**, $C_{16}H_{10}Cl_8$, M = 485.8. X-ray—preliminary study only.

Neutron diffraction data. **27**, a = 10.367, b = 14.588, c = 12.067 Å, β = 90.56°. Space group $P2_1/n$, U = 1825 Å^3, λ = 0.8482 Å, R (R') = 0.0617 (0.0429), 2865 data (120 K).

Tetrachlorotriene **30**.—Homoisodrin (**28**) was prepared by the method of Edward and Dong;[16] recrystallised from MeOH it had m.p. 192–194 °C (lit.,[16] 188–189 °C). The adduct **28** (5.66 g, 15 mmol) was heated and stirred in a mixture of *tert*-butyl alcohol (13.5 g, K_2CO_3-dried) and Na-dried THF (37.5 cm^3) whilst chips of Li metal (1.4 g, *ca.* 2.3 mol per mol Cl)[18] were introduced through a water-cooled condenser over 10–15 min. After the initial vigorous reaction had subsided (15 min) heating and vigorous stirring were continued for *ca.* 4 h after which mixture was allowed to cool. Water (150 cm^3) was added to the resulting slurry containing a little unchanged Li, followed by toluene (*ca.* 50 cm^3), the aqueous phase was separated off, toluene combined with extracts of the aqueous phase (2 × 25 cm^3) and the combined extracts were filtered through Celite filter-aid to remove a little flocculent by-product and finally washed with brine and dried (Na_2SO_4). Evaporation gave the crude hydrocarbon **29** (3.0 g, 2.49 g theory); dissolution of this in petrol, filtration from the small amount of insoluble by-product (500 mg), evaporation and distillation gave endo,endo-*tetra-cyclo*[6.2.2.1^{3,6}.0^{2,7}]*trideca*-4,9-*diene* **29** (2.0 g, 80%), b.p. *ca.* 80 °C/0.3 mmHg which solidified to a soft wax. δ 1.2 (narrow ABq system, H-11,11), 1.35 (br, m, H-12,12′,13,13′), 2.20 (br s), 2.35 (br m, H-1,8, H-3,6), 2.47 (narrow m, H-2,7), 5.37 (apparent t, H-9,10) and 5.46 (q, H-4,5); *m/z* 172 (M^+, 82%), 92 (M^+ − C_6H_8, RDA 100%), 91 ($C_7H_7{}^+$, 83%), 78 ($C_6H_6{}^{\cdot+}$, 90%) and 66 ($C_5H_6{}^+$, RDA 77%). Characterised as the *pyrazoline* **64**. (Hydrocarbon **29** appears to be sensitive to air and/or moisture; after 1 year at −20 °C in a protected stoppered flask, ^{1}H NMR spectroscopy revealed little diene remained.) Without further purification, **29** (172 mg, 1.0 mmol) and TCTD (293 mg, 1.12 mmol) were dissolved in $CHCl_3$ (2.5 cm^3); after 20 h ^{1}H NMR monitoring indicated the rapid formation of triene **30**, the presence of little **29** remained, and the appearance of **31**. [**30**, δ 1.30 (br m), 2.02 (br m, H-15,15′, H-16,16′,17,17′), 2.52 (br m, H-2,11, H-3,10), 2.90 (narrow d, H-4,9), 6.03 (t, H-13,14).] Attempts to isolate triene **30** were only partially successful, preparative TLC giving a fraction containing *ca.* 40% *dyotropomer* **31**, isolated and characterised by heating the above reaction mixture at *ca.* 60 °C for 24 h and partial evaporation, when well-formed crystals of *compound* **31** separated (50 mg), m.p. 190–191 °C: δ 0.42, 0.93 [each sym. m, AA′XX′ type, *endo* and *exo* H-13,13, H-14,14], 1.50 (collapsed AB type, H-15,15, H-16,16), 1.70 (br s, H-1,2), 1.74, 1.86 (each dt, J = 8.8 Hz, H-17,17), 2.43 (br s, H-2,11) and 3.62 (apparent t, H-3,10); *m/z* 362 (M^+, $C_{17}H_{16}{}^{35}Cl_3{}^{37}Cl^+$, 27%), 254 (RDA$^+$, 62%), 109 (RDA$^+$ + H, 100%) (Found: C, 56.1; H, 4.45. $C_{17}H_{16}Cl_4$ requires C, 56.38; H, 4.45%).

In two similar experiments hydrocarbon **29** was treated with TCTD and well resolved ^{1}H NMR signals at δ 6.03 (triene **30**) and δ 3.62 (dyotropomer **31**) monitored by integration; after 6 days/26 °C these signals became of equal intensity ($t_{\frac{1}{2}}$ **30**, ~ 144 h).

Crystal data. **31**, $C_{17}H_{16}Cl_4$, M = 362.1 (monoclinic), a = 10.372(2), b = 8.250(2), c = 18.559(4) Å, β = 98.110(15)°. Space group $P2_1/c$, U = 1572.2(5) Å^3, Z = 4, D_c = 1.53 g cm^{-3}, μ(Mo-Kα) = 7.46 cm^{-1}, $F(000)$ 744, R (R') 0.0511 (0.0697) 2509 data.

Neutron data. a = 10.2991(6), b = 8.0275(5), c = 18.5714(11) Å, α = 90.0, β = 97.569(3), γ = 90.0°. Space group $P2_1/c$, U = 1522.03 Å^3, Z = 4, λ = 1.3162 Å, $F(000)$ = 84, R (R') 0.0418 (0.0339), 2269 data, 15 K.

11-tert-*Butoxytetracyclododecadiene*, (**32**, R = Bu^{t}O).—The hexachlorocyclopentadiene adduct of 7-*tert*-butoxynorborna-

diene, **1** (R^5 = Bu^{t}O) was prepared and separated from isomers as previously described;[32] the adduct (6.55 g, 15 mmol) was dissolved in *tert*-butyl alcohol (13.5 g, K_2CO_3 dried) and Na-dried THF (37.5 cm^3), the mixture warmed and stirred and Li metal chips (1.4–1.5 g) added as previously described. The mixture was heated and stirred for 4 h, cooled, quenched with water and the product isolated by toluene extraction, drying (Na_2SO_4) and evaporation to give crude **32** (R = Bu^{t}O) (3.8 g); the viscous oily product was distilled (0.3 mmHg) to remove the brown tarry by-product, and finally redistilled to give endo, endo,anti-11-tert-*butoxytetracyclo*[6.2.1.1^{3,6}.0^{2,7}]*dodeca*-4,9-*diene* **32** (2.1 g, 60%), b.p. 102–105 °C/0.3 mmHg; δ 1.15 (s, OBu^t), 1.55 (collapsed AB system, H-12,12), 2.35, 2.58 (each quintet, H-3,6 H-1,8), 2.93 (narrow quintet, H-2,7), 3.28 (br s, H-11) and 5.26 (overlapping narrow apparent t's H-4,5, H-9,10); *m/z* 230 (M^+). Characterised as the *pyrazoline* **56**.

Cycloaddition of Dienophile **32** (R = Bu^t) *and TCTD.*—Diene **32** prepared as above (124.4 mg, 0.54 mmol) was dissolved in $CDCl_3$ (TMS) (0.9 cm^3); this solution (0.3 cm^3, 0.18 mmol **34**) was mixed with a solution of TCTD (45.7 mg, 0.18 mmol) in $CDCl_3$), to give an effective conc. of 0.36 mmol cm^{-3} in each component, and the composition monitored by ^{1}H NMR spectroscopy using the central v. sharp prominent vinylic proton signal (δ 5.22), at 4 min intervals over a period of 68 min. A graphical plot of *t vs.* $(a - x)^{-1}$ (a − *x* = peak height at time *t*) gave an acceptable second-order rate plot, and from the $(a - x)^{-1}$ intercept a value of *a*, peak-height at *t* = 0, and thus a time for half-completion of 32 min yielding a value of $k_2 = (at_{\frac{1}{2}})^{-1} = 1.45 \times 10^{-3}$ dm^3 mol^{-1} s^{-1}, at 36 °C. After this time, the ^{1}H NMR spectrum revealed two well separated vinylic hydrogen multiplets at δ 5.26 (**32**) and at δ 5.95 (**33**) in the ratio *ca.* 3:2, falling to 4:3 after a further 20 min. In a separate experiment weak signals at δ 5.26 (**32**) and 5.95 (**33**) had ratio 4:7 after 18 h, with strong signals at δ 3.86 and δ 3.52 characteristic of the dyotropomer **34**, behaviour consistent with near-equivalence in the bimolecular rate constant k_2 for cycloaddition, and k_1 for dyotropy.

Dyotropomer **34** isolated from these experiments, anti-15-tert-*butoxy*-5,6,7,8-*tetrachloropentacyclo*[10.2.1^{3,10}.0.^{2,11}0^{4,9}]*hexadeca*-4(9),5,7-*triene* had m.p. 196–197 °C; δ 1.18 (br s, Bu^{t}O), 0.41 and 1.02 (each sym. AA'XX' type, *endo* and *exo* H-13,13', H-14,14'), 1.96 (m, H-1,2), 2.08 (collapsed ABq system, H-16,16'), 3.09 (br s, H-2,11), 3.52 (apparent t, H-3,10) and 3.86 (s, H-15); *m/z* 418 (M^+, 1.1%), 362 ($M^+ - C_4H_8$, 27%) 252 (RDA, $C_9H_4Cl_4^+$, $C_9H_4{}^{35}Cl_3{}^{37}Cl^+$, 65%, hence Bu^{t}O assigned to C-15), 165 ($C_{11}H_{18}O^+ - H$, RDA, 30%, *cf. m/z* 252), 109 ($C_7H_9O^+$, RDA − C_4H_9 100%, *cf. m/z* 252) and 57 ($C_4H_9^+$ 500%) (Found: 56.65; H, 5.25. $C_{20}H_{22}Cl_4O$ requires C, 57.16; H, 5.28%).

Synthesis and Characterisation of Pyrazolines and Dyotropomeric Pyrazoles. Dyotropomeric Pyrazoline **37** and *Pyrazole* **41**.—Pyrazoline **37** and pyrazole **41**, previously prepared,[9] were crystallised by slow evaporation of CH_2Cl_2 or CH_2Cl_2–light petroleum solutions.

Crystal structure data. **37**, $C_{27}H_{22}Cl_6N_2$, *M* = 598.2, *a* = 14.187(3), *b* = 17.786(4), *c* = 21.284(4) Å, β = 94.82(4)°. Space group orthohomic *Pbca* (No. 61), *U* = 5362(2) Å^3, *Z* = 8, D_c = 1.455 g cm^{-3}, *F*(000) = 2400, μ(Mo-Kα) = 6.64 cm^{-1}, *R* (*R'*) 0.074 (0.059), 2104 data.

Pyrazole **41**, $C_{27}H_{22}Cl_6N_2$, *M* = 587.2, *a* = 8.744(4), *b* = 33.92(2), *c* = 8.788(5) Å, β = 94.82(4)°. Space group, monoclinic $P2_1/n$ (non-standard No. 14), *U* = 2597(2) Å^3, *Z* = 4, D_c = 1.502 g cm^{-3}, F(000) = 1200, μ(Mo-Kα) = 6.85 cm^{-1} *R* (*R'*) = 0.086 (0.094), 2303 data. Some disorder in the heterocyclic ring reduces the precision of the data. See below for discussion of ^{1}H NMR spectra and X-ray structural correlations.

Pyrazoline **39** obtained in earlier work[9] was crystallised as above.

Crystal data. $C_{26}H_{19}Cl_7N_2$, *M* = 607.3, *a* = 14.164(4), *b* = 17.763, *c* = 21.287 Å. Space group *Pbca*, *U* = 5356(2) Å^3, *Z* = 8, D_c = 1.506 g cm^{-3}, *F*(000) = 2464.0, μ(Mo-Kα) = 7.70 cm^{-1}, *R* (*R'*) = 0.0436 (0.0540), 2667 data.

Pyrazoline Synthesis. Compounds **44**, **45**, **46**.—1,3-Diphenylnitrilimine adducts of *syn*-, *anti*- and bis-dechloroisodrin derivatives **19**, **20** and **21** were made and purified essentially as for analogue **36**;[9] endo,endo,exo-1,11,12,13-anti-14-*pentachloro*-5,7-*diphenyl*-5,6-*diazapentacyclo*[9.2.1.1^{3,9}.0^{2,10}.0^{4,8}]-*pentadeca*-6,12-*diene* **44**, m.p. 242–243 °C, δ 1.56, 1.60 and 1.78, 1.82 (each m, ^2J = 10.9 Hz, H-15,15'), 3.34 (m, collapsed AB system, H-2,10), 2.86 and 2.99 (each narrow nm, H-9, H-3), 3.96 and 4.44 (each dd ^3J = 9.16 and *ca.* 1.5 Hz, H-8, H-4), 4.30 (sharp s, H-14), 6.8–7.7 (four complex m, 2 Ph); *m/z* 522 (M^+, 524 = 100%), 487 (M^+ − Cl), 77 ($C_6H_5^+$ 67%), 285 ($M^+ - C_5HCl_5$ − H, RDA 66%), 258 (RDA$^+$ 19%); λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) 362–364 (20 265) (Found: C, 57.2; H, 3.75; N, 5.3. $C_{25}H_{19}Cl_5N_2$ requires C, 57.23; H, 3.65; N, 5.34%).

The *syn*-14-chloro isomer, *pyrazoline* **45**, m.p. 281–282 °C, δ 1.45, 1.49 and 1.81, 1.85 (each m, ^2J = 10.99 Hz, H-15,15'), 2.94, 3.08 (overlapping m, H-2,10 and H-3,9), 3.96 and 4.4 (each dd, ^3J = 9.16, and *ca.* 1.5 Hz, H-8, H-4) and 4.53 (sharp s, H-14); *m/z* 522 (M^+, 524 = 100%), major fragment ions identical with those from **44**, with similar abundances; λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) 362–364 (18 724) (Found: C, 57.05; H, 3.9; N, 5.2. $C_{25}H_{19}Cl_5N_2$ requires C, 57.23; H, 3.65; N, 5.34%).

The 14,14-bisdechloro analogue, *pyrazoline* **46**, m.p. 273.5 °C, δ 1.52, 1.56 and 1.77, 1.81 (each m, ^2J = 10.62 Hz, H-15,15'), 2.79, 2.82 and 2.84, 2.86 (tending to AB system, 2.84, 2.86 *syn* H, more shielded and broader than 1.77, 1.81, ^6J coupling to *syn* H-15 unresolved), 3.2 (m, H-2,10), 2.96 [m, and near 2.83 (underlying H-14 *syn*), H-3,9], 3.98 (dd, ^3J = 9.15, *ca.* 1.5 Hz, H-8), 4.46 (dd, ^3J = 9.15, 1.1 Hz, H-4) and 6.84–7.72 (four complex m, 2 Ph); *m/z* 488 (M^+, 490, 100%), 453 (M^+ − Cl), 77 ($C_6H_5^+$), 285 ($M^+ - C_5H_2Cl_4$ − H, RDA 44%) and 258 (RDA$^+$ 24%); λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) 364–366 (21 990) (Found: C, 61.55; H, 4.2; N, 5.7. $C_{25}H_{20}Cl_4N_2$ requires C, 61.25; H, 4.11; N, 5.71%).

Dyotropomeric Pyrazoles **47**, **48**, **49**.—These were made by mild thermolysis (PhBr, b.p., N_2[9]) of pyrazolines **44**, **45**, **46**, respectively, and purified by preparative TLC and recrystallisation (CH_2Cl_2–light petroleum or CH_2Cl_2–MeOH). endo,-endo-1,11,12,13-anti-14-*pentachloro*-5,7-*diphenyl*-5,6-*diaza-pentacyclo*[9.2.1.1^{3,9}.0^{2,10}.0^{4,8}]*pentadeca*-4(8),6-*diene* **47**, m.p. 280–281 °C, δ 2.26, 2.29 and 2.63, 2.66 [each m, ^2J = 8.79 Hz *anti*- and *syn*-H-15 (confirmed by spin decoupling, *syn*-H-15 is spin-coupled to *syn*-H-14, ^6J = 0.73 Hz, and deshielded by pyrazole ring)], 3.58 and 4.40 (each d, *J* = 7.51 Hz, H-12,13), 4.74 (d, ^6J = 0.73 Hz, *syn*-H-14), 3.80–3.97 (overlapping cm, H-2,10 and H-3,9), 7.2–8.0 (cm, 2 Ph); *m/z* 522 (M^+, 524, 46%), 487 (M^+ − Cl, 489 89%), 452 ($M^+ - Cl_2$, 454, 100%), 77 ($C_6H_5^+$, 84%), 258 (RDA, $M^+ - C_7H_5Cl_5$, 57%) and 285 (RDA 23%); λ_{max} transparent at 360–364 nm (representative UV of analogues of pyrazoles have λ_{max}280–300 nm)[9] (Found: C, 56.75; H, 3.65; N, 5.25. $C_{25}H_{19}Cl_5N_2$ requires C, 57.23; H, 3.65; N, 5.34%).

48, m.p. 308–309.5 °C, δ 2.07, 2.11 and 2.59, 2.63 (each apparent t, *anti*- and *syn*-H-15), 3.57 and 4.35 (each dd, ^3J = 7.33, ^4J = 1.5 Hz, H-13 and H-12 coupled to *anti*-H-14), 3.88 and 3.94 (each m, H-9 and H-3), *ca.* 3.43–3.56 (complex m overlapping H-13, H-2,10) and 7.34–7.92 (four complex m, 2

Ph); *m/z* 522 (M^+, 524, 100%) and fragment ions otherwise similar to pyrazole **47**; λ_{max} transparent at 360–364 nm (Found: C, 56.85; H, 3.8; N, 5.25. $C_{25}H_{19}Cl_5N_2$ requires C, 57.23; H, 3.65; N, 5.34%).

49, m.p. 279–281 °C, δ 2.19, 2.22 (each t, ^2J = 8.79, ^3J = 1.5 Hz) and 2.59, 2.63 (each q, ^2J = 8.79, *anti-* and *syn*-H-15), 2.42, 2.46 (each t, ^2J = 9.89, ^4J = 2.2 Hz) and 2.91, 2.95 [each d, ^2J = 9.89, ^6J = 0.73 Hz, *anti-* and *syn*-H-14 (coupled to H-12,13- and *syn*-H-15, respectively)], 3.44 and 3.47 [each d, ^3J = 6.59, ^4J = 2.2 Hz, H-12 (or 13)] 3.65, 3.69, 3.73 obscured, 3.78 (each d, ^3J = 12.46 and 3.48 Hz, AB type further coupled, *cf.* pyrazole **41**, H-2,10), 3.77 and 3.82 (each m, H-9 and H-3) and 4.24, 4.26 [each d, ^3J = 6.59, ^4J = 2.2 Hz, H-13 (or 12)]; *m/z* 488 (M^+), 453 (M^+ − Cl, 455, 100%), 77 ($C_6H_5^+$, 72%), 258 (RDA, $M^+ - C_7H_6Cl_4$, 77%) and 285 (RDA, 59%); λ_{max} transparent at 360–364 nm (Found: C, 61.4; H, 4.35; N, 5.75. $C_{29}H_{20}Cl_4N_2$ requires C, 61.25; H, 4.11; N, 5.71%).

Pyrazolines **56** *and* **57** *and Dyotropic Isomers* **58**, **59**.—*tert*-Butoxyisodrin (**1**; R^5 = Bu^{t}O) (218 mg, 0.5 mmol) was heated in PhBr (*ca.* 1 cm^3) with 2,5-di(*p*-chlorophenyl)tetrazole[33] (145 mg, 0.5 mmol) under N_2 for 18 h (TLC monitoring indicating slow consumption of dipolarophile **1**, R^5 = Bu^{t}O). N_2 blow-off of PhBr and repeated preparative TLC (1:1 CH_2Cl_2–light petroleum, then CH_2Cl_2 for the partially separated mixture finally gave after recrystallisation of fractions (×2) *pyrazoline* **56** (54 mg, 16%), m.p. 243–245 °C (decomp.), pyrazole **58** (44 mg, 13%), m.p. 264–265 °C (decomp.) and an orange dimer of 1,3-di-(*p*-chlorophenyl)-nitrilimine (50 mg, 38%), m.p. 249–251 °C (decomp.) and a little unchanged dipolarophile (36 mg, 11%).

endo,endo,exo-anti-15-tert-*butoxy*-1,11,12,13,14,14-*hexachloro*-5,7-*di*(p-*chlorophenyl*)-5,6-*diazapentacyclo*[9.2.1.1^{3,9}.0^{2,10}.0^{4,8}]*pentadeca*-6,12,*diene* **56**, δ 1.03 (s, Bu^{t}O), 2.55 and 2.69 (each m, H-9, H-3), 6.07 (sym. m, AB system further coupled to H-3,9, H-2,10), 3.82 and 4.27 (each d, ^3J = 10.44 Hz, H-8, H-4), 4.19 (br s, H-15) and 6.97–7.59 (2 × AA′XX′ m, 2 × *p*-ClC_6H_4); *m/z* 700 (M^+, 704, 24%), 643 ($M^+ - C_4H_9$, 647, 7%), 609 ($M^+ - C_4H_8$ − Cl, 15%), 339 (4%), 289 (6.3%) and 57 (Bu^{t+}, 100%); λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) 364–366 (17 778) (Found: C, 49.65; H, 3.5; N, 4.0. $C_{29}H_{24}Cl_8N_2O$ requires C, 49.75; H, 3.45; N, 4.00%).

Pyrazole, **58**, δ 1.17 (s, Bu^{t}O), 3.50 and 4.25 (each d, ^3J = 8.5 Hz, H-12,13), 3.52 (br m, H-3,9), 3.78 (narrow m, H-2,10, overlapping H-14) and 7.05–7.70 (2 × AA′XX′ m, 2 × *p*-ClC_6H_4); *m/z* M^+ absent, 643 ($M^+ - C_4H_9$, 647, 32%), 609 ($M^+ - C_4H_8$ − Cl, 21%) and 339 (21%); λ_{max} transparent at 360–364 nm (Found: C, 49.85; H, 3.55; N, 3.95. $C_{29}H_{24}Cl_8N_2O$ requires C, 49.75; H, 3.45; N, 4.00%). This same compound was obtained by mild thermolysis (PhBr, b.p., N_2) of pyrazoline **56**.

2,3,5,6-Tetra-(*p*-chlorophenyl)-3,6-dihydro-1,3:4,6-tetrazine, m.p. 249–251 °C (decomp.), *m/z* 526 (M^+, 528, 100%), bis(*p*-chlorophenyl)nitrilimine dimer.

Hexadechloropyrazoline **57**.—Dipolarophile **32** (R = OBu^t) (230 mg, 1 mmol), was heated with 2,5-diphenyltetrazole (222 mg, 1 mmol) in PhBr (3.5 cm^3, under N_2) for a total of 6.5 h (TLC monitoring). The solvent was blown off (N_2) and the mixture of products was subjected to repetitive preparative TLC (Type H silica gel, starch binder, CH_2Cl_2–light petroleum, 3:20) to give *pyrazoline* **57** (53 mg, 12%), recrystallised from light petroleum (41 mg), m.p. 237–238.5 °C, δ 1.15 (s, Bu^{t}O), 1.53 (m, H-15,15), 2.49 (m, H-2,10), 2.68 (m, H-3,9), 3.47 and 3.75 (each d of narrow m, $^3J \cong 9$ Hz, H-4, H-8), 3.47 (narrow m, H-14), 5.92 (apparent t, H-12,13) and 7.2–8.0 (m, 2 C_6H_5); *m/z* 424 (M^+, 100%), 368 ($M^+ - C_4H_8$, 65%), 367 ($M^+ - C_4H_9$, 53%), 339 (68%), 258 (RDA$^+$, $M^+ - C_{11}H_{18}O$, 66%) and 57 (Bu^{t+}, 78%); λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) 368–370 (21 447) (Found: C, 81.95; H, 7.6; N, 6.55. $C_{29}H_{32}N_2O$ requires C, 82.03; H, 7.59; N, 6.59%).

The remaining product appeared to be a mixture containing *pyrazole* **59** and two unidentified compounds. Pyrazole **59** (17 mg, 90%) was obtained by mild thermolysis of pyrazoline **57** (19 mg, PhBr, b.p., N_2, 24 h) and preparative TLC (5:1 light petroleum–Et_2O), m.p. 183.5–185 °C after recrystallisation (light petroleum). δ 1.21 (s, Bu^{t}O), 0.28 [c m, *endo*-H-12 (or 13)], 0.90–1.06 [c m, *endo*-H-13 (or 12) and *exo*-H-12,13], 1.99 (br s, H-1,11), 2.32 (dt, J = 8.1 Hz, H-15), 2.51 (dq, J = 8.1 and ~ 1 Hz, *syn*-H-15, coupled to H-14), 3.16 and 3.29 (each dt, J = 11.3, ~ 4 Hz, H-2,10), 3.48 and 3.54 (each m, H-3,9), 3.90 (br s, H-14) and 7.22–7.95 (m, 2 C_6H_5); *m/z* 424 (M^+, 51%), 367 ($M^+ - C_4H_9$, 55%), 368 ($M^+ - C_4H_8$, 34%), 258 ($M^+ - C_{11}H_{18}O$, RDA, 100%), 77 ($C_6H_5^+$, 58%) and 57 (Bu^{t+}, 53%); λ_{max} transparent at 368–370 nm (Found: M^+, 424.2481. $C_{29}H_{32}N_2O$ requires *M*, 424.2514).

Pyrazolines **60**, **61**, **64**, *and Dyotropomeric Pyrazoles* **62**, **63**, **65**.—Attempted synthesis of pyrazolines **60** and **61** by the usual tetrazole thermolysis methods described above gave their dyotropomers (**62**, **63**); product-analysis by preparative TLC revealed < 1% pyrazolines. Whilst successful with isodrin, **1** [the photolysis of 2,5-di(*p*-chlorophenyl)tetrazole (1.45 g, 5 mmol) and isodrin (3.65 g, 10 mmol) in benzene (100 cm^3) with a medium-pressure mercury arc (125 W, 20 h) with water cooling and acetone washing of the tarry solid product giving pyrazoline **38**[9] (recrystallised, 1.37 g, 44%)] the photochemical method[34] failed to produce a significant adduct **60** or **61** when homoisodrin **28** was employed in similar experiments. The following procedure gave small but useful amounts of the required pyrazolines **60**, **61**. Homoisodrin **28** (570 mg, 1.5 mmol) was ground to a fine powder with 2,5-diphenyltetrazole 1.332 g, 6 mmol), the mixture moistened with xylene (0.5 cm^3) in an ampoule suspended in a xylene vapour bath (temp. ≤140 °C), was heated for 3 h. The crude product solidified on cooling, and was repeatedly extracted with hot MeOH (5 × 20 cm^3) to remove **28** and unchanged tetrazole, leaving crude *pyrazoline* **60** admixed with *pyrazole* **62**; preparative TLC (5:1 CH_2Cl_2–light petroleum) resolved the mixture giving endo,endo,exo-1,11,12,13,14,14-*hexachloro*-5,7-*diphenyl*-5,6-*diazapentacyclo*-[9.2.1.2^{3,9}.0^{4,8}.0^{2,10}]*hexadeca*-6, 12-*diene* **60** (88 mg, 10% after recrystallisation, CH_2Cl_2–light petroleum), m.p. 332–333 °C (concomitant dyotropy and decomp.) and pyrazole isomer endo,endo-1,11,12,13,-14,14-*hexachloro*-5,7-*diphenyl*-5,6-*diazapentacyclo*[9.2.1.2^{3,9}.0^{4,8}.0. ^{2,10}]*hexadeca*-4(8),6-*diene* **62** (80 mg, 9.4% after recrystallisation), m.p. 331–333 °C (decomp.).

60, δ 1.57, 1.90 (m, H-15,15 H-16,16), 2.48, 2.64 (each quintet, H-9, H-3), 3.03, 3.06, 3.09, 3.11 (each d, ^3J = 10.99, 2.5 Hz converging AB system further coupled, H-2,10), 3.84, 3.87 (each dm, ^3J = 12.7 Hz, H-8), 4.40, 4.43 (each d, ^3J = 12.7, ~ 2.5 Hz, H-4) and 6.8–7.6 (6 m, 2 × C_6H_5); *m/z* 572 (M^+, 574, 97%), 537 (M^+ − Cl, 44%), 268, 269, 270, 271, 272 (dyotropic 2 H, shift, RDA, $C_{19}H_{16}N_2^+$ with loss of 1–4 H, 270, 73% and 271, 100%); λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) 362.2 (18 914) (Found: C, 54.7; H, 3.7; N, 4.95. $C_{26}H_{20}Cl_6N_2$ requires C, 54.48; H, 3.52, N, 4.88%).

Crystal data. **60**, $C_{26}H_{20}Cl_6N_2$, M = 573.1, a = 10.408(3), b = 19.990(4), c = 12.443(3) Å, β = 100.81(2)°. Space group $P2_1/n$, U = 2542.9(11) Å^3, Z = 4, D_c = 1.497 g cm^{-3}, $F(000)$ = 1168, R (R') 0.043 (0.0403), 1889 data.

62, δ 1.53, 1.84 (each AB type m, H-15,15 H-16,16), 3.11, 3.16, 3.19, 3.24 (each d, ^3J = 12.45, 2.3 Hz converging AB system further coupled, H-2,10), 3.84, 3.88 (each m, H-9, H-3) and 4.02, 4.67 (each d, ^3J = 8.79, H-12,13); *m/z* 572 (M^+, 97%), 537 (M^+ − Cl, 44%), 268, 269, 270, 271, 272 (as for **60**); λ_{max} transparent at 362 nm (Found: C, 54.55; H, 3.7; N, 4.95%).

Crystal data. **62**, $C_{26}H_{20}Cl_6N_2$, M = 573.1, a = 17.889(4), b = 17.713(4), c = 7.715(2) Å. Space group *Ama*2, U = 2444.7(11) Å^3, Z = 4, D_c 1.557 g cm^{-3}, F(000), 1168 R (R') 0.0332 (0.0359), 1039 data.

In a similar experiment, homoisodrin (1.5 mmol) was exposed to 2,5-di(*p*-chlorophenyl)tetrazole (1.74, 5.9 mmol) and the crude thermolysis product was taken up in CH_2Cl_2, concentrated and cooled, excess tetrazole crystallising (1.35 g); trituration of the evaporated residue with further CH_2Cl_2, and boiling with MeOH removed tetrazole and remaining **28** to give crude *pyrazoline* **61** (with traces of *pyrazole* **63**) (139 mg, 14%). Preparative TLC (5:1 CH_2Cl_2–light petroleum) gave the *pyrazoline* **61** (81 mg, 8.5%) bis(aryl)tetrazole (38 mg) and **28** (10 mg).

Recrystalllised from CH_2Cl_2–light petroleum, endo,endo,-exo-1,11,12,-13,14,14-*hexachloro*-5,7-*di*(p-*chlorophenyl*)-5,6-*diazapentacyclo*-[9.2.1.2^{3,9}.0^{4,8}.0^{2,10}]*hexadeca*-6,12-*diene* **61**, m.p. 253–255 °C; kept 10 min at 280 °C and cooled, the solidified m.p. sample remelted at 312–314 °C (*cf.* **63**); δ 1.53, 1.83 (each m, H-15,15, H-16,16), 2.43, 2.59 (each quintet, H-9, H-3), 3.02, 3.06, 3.08, 3.12 (each d, ^3J = 10.9 and ~2.2 Hz, converging AB system, H-2,10), 3.79, 3.84 (each dm, ^3J = 12.5 and 2.8 Hz, H-8), 4.35, 4.40 (each br d, ^3J = 12.5, H-4 centred at 6.96, 7.24 and 7.37, 7.52, 2 × AA'XX' m, 2 × *p*-ClC_6H_4); m/z 642 (M^+, 646, 100%), 607 (M^+ − Cl, 25%), 605 (M^+ − Cl − 2 H, 23%), 344, 343, 342, 341, 340, 339 and 338 (overlapping isotopic ion-clusters for RDA, $C_{19}H_{16}N_2Cl_2^+$ and loss of 1–4 H, *cf.* **60**); λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) 370.3 (23 472) and 325sh (8273) (Found: C, 48.6; H, 3.05; N, 4.3. $C_{26}H_{18}Cl_8N_2$ requires C, 48.63; H, 2.82; N, 4.36%).

Pyrazole **63**. Homoisodrin **28** (758 mg, 2 mmol) was heated with di(*p*-chlorophenyl)tetrazole (291 mg, 1 mmol) in PhBr (3 cm^3) at *ca.* 160 °C for a total of 10 h with TLC monitoring, adduct formation appearing slower than for isodrin; light petroleum dilution of the cooled mixture delivered crude pyrazole **63** (270 mg) and recrystallisation (CH_2Cl_2–light petroleum) gave pure **63** (202 mg, 31%), m.p. 316–318 °C, δ 1.44–1.60 (m) and 1.84 (AB-type m, H-15,15 H-16,16), 3.10, 3.14, 3.18, 3.22 (each d, ^3J = 12.45, ~2.3 Hz, H-2,10), 3.78, 3.81 (each m, H-9, H-3), 3.88, 4.52 (each d, ^3J = 8.79 Hz, H-12,13) and 7.43–7.74 (2 AA'XX', 2 × *p*-ClC_6H_4); m/z major ions identical with **61**; λ_{max} transparent at 370 nm (Found: C, 48.9; H, 3.0; N, 4.4%).

Crystal data. **63**, $C_{26}H_{18}Cl_8N_2$, M = 642.0, a = 22.808(6), b = 9.605(3), c = 14.231(3) Å, β = 100.75(2)°. Space group $P2_1/c$, U = 3063.5(14) Å^3, Z = 4, D_c = 1.392 g cm^{-3} F(000) = 1296, R (R') 0.0490 (0.0587), 2419 data.

Hexadechlorohomoisodrin–Di(p-*chlorophenyl*)*nitrilimine Adduct Formation. Pyrazoline* **64** *and Pyrazole* **65**.—Hexadechlorohomoisodrin **29** (345 mg, 2 mmol) was heated with 2,5-di(*p*-chlorophenyl)tetrazole (291 mg, 1 mmol) in PhBr (2 cm^3, N_2) for 3.5 h; N_2 blow-off of solvent gave a crude product which was subjected to preparative TLC (3:1 light petroleum–CH_2Cl_2) and resolved into several minor unidentified fractions with *pyrazoline* **64** as the major fraction (238 mg, 55%), m.p. 230–232 °C (from CH_2Cl_2–light petroleum); δ 1.40 (m), 2.50 (br m) (overlapping H-1,11, H-3,9, H-15,15, H-16,16), 2.05 (br s collapsed AB type, H-2,10), 3.56, 4.02 (each br d, J = 9.0 Hz, H-8, H-4), 6.05 (apparent t, H-12,13) and 6.7–7.7 (overlapping AA'XX' m, 2 × *p*-ClC_6H_4); m/z 434 (M^+, 65%) 326 (M^+ − C_8H_{12}, dyotropic 2 H shift, RDA 100%); λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) 379 (23 857) (Found: C, 71.9; H, 5.7; N, 6.35. $C_{26}H_{24}Cl_2N_2$ requires C, 71.72; H, 5.56; N, 6.43%).

Thermolysis of Pyrazoline **64**. Pyrazoline **64** (40 mg) was heated in PhBr (*ca.* 1.5 cm^3, N_2) at the b.p. (156 °C) for a total of 98 h; the clean product solution was resolved by preparative TLC 3:1 light petroleum–CH_2Cl_2, into two fractions, pyrazoline **64** (22 mg) and *pyrazole* **65** (15 mg) (92.5% recovered product):

$$k_1 = t^{-1} \ln \frac{a}{a-x} \cong 2.88 \times 10^{-6} \ln \left(\frac{40}{22}\right) \cong 1.69 \times 10^{-6}\ s^{-1}.$$

Dyotropomer **65**, from CH_2Cl_2–light petroleum, m.p. 183–185 °C, δ 0.70, 0.85 (each m, H-12,12, H-13,13), 1.50 (m) overlapping 1.58 (m, H-15,15, H-16,16, H-1,11), 1.90, 2.19 (each dm, ^2J = 8 Hz, H-14,14), 2.46 (m, H-2,10), 3.50 (m, H-3,9) and 7.0–7.9 (overlapping AA'XX' signals, 2 *p*-ClC_6H_4); m/z see compound **64** (Found: M^+, 434.1290. $C_{26}H_{29}Cl_2N_2$ requires M, 434.1216); λ_{max} transparent at 379 nm.

PDKIE Analysis.—[^{2}H]*Isodrin* (**1**). Deuterium oxide (25 cm^3, 1.375 mmol) was cooled in an ice-bath and sodium metal chips (2.48 g, 110 mmol) were added over 0.5 h. Freshly cracked cyclopentadiene (2.02 g, 31 mmol) was added to this solution and the mixture was stirred for 24 h and finally heated for a further 24 h under reflux. The product was extracted with dichloromethane (3 × 50 cm^3), the extracts washed with brine and then dried (Na_2SO_4); solvent removal gave a pale yellow liquid (1.36 g, 9.6 mmol, 63%), 70–75% ^{2}H-labelled dicyclopentadiene; δ_D(61.4 MHz) (IUPAC numbering) 6.02 (D-9), 5.98 (D-8), 5.55 and 5.51 (D-3, D-4), 3.20 (D-2), 2.87 (D-1), 2.77 (D-7), 2.70 (D-6), 2.15 and 1.58 (D-5,5'), 1.45 and 1.27 (D-10,10'); ν_{max}(thin film)/cm^{-1} 2934vs and 2191vs (C–H and C–D stretch). This product was thermally cracked in a short-path distillation apparatus and the [^{2}H]cyclopentadiene produced was added to 1,2,3,4,7,7-hexachloronorborna-2,5-diene (1.54 g, 5.15 mmol) and the mixture heated in a screw-cap Youngs pressure tube at 130 °C (oil bath) for 24 h. More [^{2}H]-cyclopentadiene was added and heating was continued several hours. Dry flash chromatography of the product (silica, 30% v/v dichloromethane–petrol) and solvent removal gave [^{2}H]-**1** and unchanged [^{2}H]dicyclopentadiene; the latter was removed with light petroleum and the remaining solid was recrystallised (methanol) to give colourless crystals of **1** with 70% ^{2}H incorporation (1.08 g, 2.96 mmol, 57%), m.p. 235–235.4 °C (**1**, m.p. 246 °C); δ_D(61.4 MHz), 6.04 (D-9,10), 3.00 (D-3,6), 1.75 and 1.53 (D-12,12') [^{2}H incorporation was estimated from the ratio of the residual ^{1}H signal intensities in the ^{1}H NMR spectrum (400 MHz) to that of the 100% ^{1}H signal due to ring-junction protons H-2 and H-7 at δ 3.36, which derive from the vinyl protons in hexachloronorbornadiene dienophile].

^{2}H-*Triene* **5**. 70% [^{2}H]-**1**, prepared as above, was converted into 70% ^{2}H-triene **5** by the sequence[5a,9] (*i*) cycloaddition of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene and (*ii*) hydrolysis of the resulting adduct to the norbornen-7-one derivative followed by (*iii*) decarbonylation in boiling carbon tetrachloride for *ca.* 1 h.

Isotopic-isomer Enrichment of ^{2}H-*Triene* **5**. ^{2}H-Labelled triene **5** prepared as above (192.6 mg) was dissolved in decalin (5–6 cm^3) and the solution heated under N_2 in an ampoule immersed in a thermostat at 95 °C, for 6.6 h; on cooling, the solution deposited the dyotropomer **9** of **5** (79 mg) and the decalin phase was removed, combined with several light petroleum washings of the separated solid **9** and evaporated, and the decalin blown off (N_2) at 90–95 °C over 1 h and at 80 °C, 1 h (water bath, total heating time *ca.* 8 half-lives for [^{1}H]-**5**). Crude ^{2}H-triene **5** was subjected to preparative TLC (2:1 light petroleum–CH_2Cl_2) to give enriched ^{2}H-triene **5** (71 mg) and dyotropomer **9** (36 mg, total recovered **9**, 115 mg). ^{2}H-Enriched triene **5**, prepared in this manner, had m.p. 293–294 °C (concomitant rearrangement 2 H);[5a,9] m/z 550 ($M^{\bullet+}$, ^{1}H, ^{2}H, ^{35}Cl and ^{37}Cl ion cluster) (^{2}H, %) $^2H_3$ 0.82, $^2H_4$ 3.41,

$^2H_5$ 23.12, $^2H_6$ 72.6); ^1H NMR (400 MHz) (^1H, %) H-3,10 6.7; H-16,16' 7.7; H-4,9 2.4; H-2,7 100; δ_D(61.4 MHz) 1.62, 2.02 (D-16,16'), 3.04 (D-3,10) and 3.11 (D-4,9). After 8 × $\tau_{\frac{1}{2}}$ calculated depletion, Table 1 data, the ^1H-triene **5** = 99.6%; observed (at each of C-4,9) 98.8%. This compound had the expected UV absorption maxima in the 280–320 nm range characteristic of ^1H-triene **5**.[5a,9] For kinetic experiments an absorption maximum at 308.5 nm (PE 552 spectrometer), where the dyotropomer **9** is transparent, was used to assay composition.

~70% [^2H]*Pyrazoline* **38**.—This compound was prepared from [^2H]isodrin (**1**) samples obtained as above by heating with 2,5-di(*p*-chlorophenyltetrazole)[33] (PhBr, N_2, reflux) as previously described.[9a] Trial kinetic runs with the product-solution in decalin at 207.6 °C showed marked initial convex curvatuve for $\log[D_0 - D_\infty/D_t - D_\infty]$ *vs.* *t*, finally becoming approximately linear after *ca.* 8 h (4.6 × $t_{\frac{1}{2}}$).

Isotopic-isomer Enrichment [^2H]*Pyrazoline* **38**.—The ^2H-labelled pyrazoline (64 mg) was dissolved in warm decalin (5–6 cm^3) in an ampoule, and the solution subject to four freeze–thaw cycles (as for samples for kinetic experiments) in the sequence: freeze (−196 °C), vacuum (0.3 mmHg), N_2, warm to liquify sample, then partial vacuum until gas evolution ceased. The ampoule was finally sealed under vacuum whilst the sample was cooled at −196 °C. The ampoule was immersed in a thermostat and heated at 207.6 °C for 14.9 h (*ca.* 8 half-lives for [^1H]-**38**) and the product isolated by N_2 blow-down at 95 °C (water-bath). Preparative TLC (silica gel, 5:1 light petroleum–dichloromethane) gave rearrangement product, dyotropomer **42** (43 mg) and ^2H-enriched pyrazoline **38** (19.8 mg), m.p. 274–276 °C (concomitant 2 H);[9] 624 ($M^{\cdot+}$ ^1H, ^2H, ^{35}Cl and ^{37}Cl ion-cluster) (^2H, %) $^2H_3$ 3.79, $^2H_4$ 6.31, $^2H_5$ 16.9, $^2H_6$ 61.5. ^1H NMR (400 MHz) (^1H, %) H-3,9 6.95; H-15,15' 9.6; H-4,8 3.7; δ_D(61.4 MHz) 1.51 and 1.74 (D-15,15'), 2.94 (D-3,9), 3.88 and 4.36 (D-8,4). After 8 × $\tau_{\frac{1}{2}}$ calculated depletion, (Table 4 data), [^1H]pyrazoline **38** = 99.6%; observed (at each of C-4,8) 98.15%. For kinetic runs, carried out as previously,[9] solutions of [^2H]pyrazoline **38** were assayed at 372 nm, pyrazole product being transparent at this wavelength.

^1H *NMR–X-Ray Structure Correlations.—Pyrazoline* **37** *and pytrazole* **41**. The crystal structure data for pyrazoline **37** and dyotropomer **41** show greater molecular distortion for compound **41** compared with **37**. This prompted a close scrutiny of the ^1H NMR spin-coupled system H-2,10 with H-3,9 for both isomers. Solid-state asymmetry is most obvious in the torsion angles H(2)–C(2)–C(10)–H(10) which, whilst having a large uncertainty, is not zero (5.7 ± 5.4°). The atomic positions of C(1), C(11), and C(3), C(9) are much more accurately located, with torsion angles 1.5° and 2.8° (±0.7°), respectively. Intermolecular distances are more disparate in pyrazole **41** than in pyrazoline **37** with d_{CH} C(4)···H(13) 2.22 Å and C(8)···H(12) 2.33 Å, with torsion angles H(2)–C(2)–C(10)–H(10) 14.4 ± 7.5°, and C(1)–C(13)–C(12)–C(11) 3.1 ± 0.9°. The GX270, GX500 and GSX500 ^1H NMR spectra of **37** and **41** exhibit an obvious significant difference for protons H-2,10 in the two isomers as might be expected from the above differential distortion effects, the concomitant observed frequency difference resulting in a clearly resolved AB system of narrow doublets for these protons in **41** (δ 3.658, 3.672; 3.703, 3.717; 3.773, 3.787; 3.818, 3.832, $^3J_{AB}$ = 1.21 Hz, ^3J coupling to H-3,9 = 3.85 Hz, $J_{AB}/\Delta\nu_{AB}$ = 0.42). For the less distorted pyrazoline **37** the H-2,10 environmental difference must be significantly smaller, whilst their mutual coupling changes little. Simulation of the second-order spectra, carried out using the NUMARIT package[35] indicates that $J_{AB}/\Delta\nu_{AB}$ is an order of magnitude larger (3.03) for **37**. The result is that the two proton signal collapses to an ill-resolved multiplet, with only partial resolution at 500 MHz. The NMR parameters are thus consistent with asymmetry in these compounds persisting in solution.

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