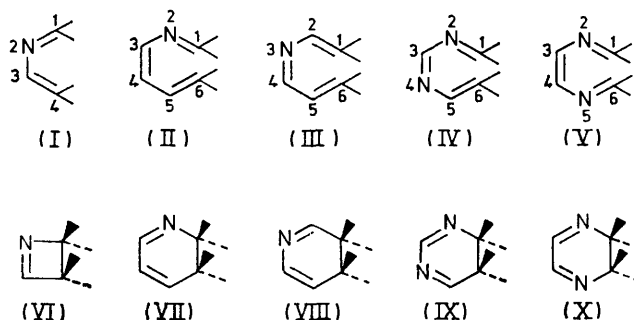


Orbital Correlations for Aza-derivatives of Butadiene and Hexatriene

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Molecular orbital theory predicts that electrocyclic reactions of 2-azabutadiene and of aza- and diaza-hexatrienes should proceed along a pathway similar to that of their hydrocarbon analogues. Thermal reaction of 2-azabutadiene should be conrotatory, while photochemical excitation should lead to a disrotatory cyclisation mechanism. The reverse is expected for the aza- and diaza-hexatrienes. Some experimental evidence is presented to support these observations.

THE theory of electrocyclic reactions of butadiene and hexatriene was recently studied by Woodward and Hoffman.¹ During our studies on pyrimidines, purines, and pteridines it became necessary to derive some guiding rules for the pathway of electrocyclic reactions of the aza-derivatives of these hydrocarbons [compounds (I)–(V)]. We were aware that introduction of nitrogen atoms into butadiene and hexatriene systems may



cause complications in the theoretical analysis for the following reasons. (1) The all-planar conformations of butadiene, hexatriene, and their cyclic isomers, cyclobutene and 1,3-cyclohexadiene, show both C_2 -axis and C_s symmetries.² In the present series, however, both these features are manifested only by compounds (V) and (X). Therefore, it would be very difficult to construct a correlation diagram, as suggested by Longuet-Higgins and Abrahamson.³

(2) The predictions of Woodward and Hoffmann are based on the fact that the highest occupied and the lowest empty MO's (HOMO and LUMO) of butadiene and hexatriene are of a π character. Introduction of nitrogen atoms into the framework of these hydrocarbons may change the situation radically. Using the CNDO/2 method⁴ Pullman⁵ recently concluded that for polyaza-heterocycles, e.g., pyrimidines and purines, 'there appears a definite mingling of the highest occupied σ - and π -levels'. Therefore it is not certain whether the 'frontier'⁶ orbitals of compounds (I)–(X) possess the π -orbital-symmetry necessary for the application of the Woodward-Hoffmann treatment. Moreover, it has been shown by Kikuchi,⁷ using the CNDO/2 algorithm,

that in systems with 'strong mixing of π - and σ -orbitals, the correlation diagram relating only π -orbitals is of little value'.

(3) Introduction of nitrogen into butadiene and hexatriene opens up the new possibility of n - π^* excitation and lone-pair interactions, which are not encountered in the parent hydrocarbons. It is yet unknown in which way the orbital symmetries would be influenced by such interactions; however, these may not be negligible.⁸

(4) The azomethine groups C=N are highly polarised; therefore, net charges, bond orders, and dipole moments, rather than merely orbital symmetries, should now be considered as possible factors contributing to the course of the electrocyclic reaction.

In view of the difficulties expected in the analysis of the orbital correlations of compounds (I)–(X), it was decided to base our approach on wave functions obtained by the simple HMO method, from which the nodal properties of the MO's are deduced. All the results presented here were substantiated by more 'accurate' calculations including both σ - and π -electrons, viz., CNDO/2 and extended Hückel.⁹ In this all-valence-electron calculation it was found that HOMO and LUMO of compounds (I)–(V) are indeed of π -symmetry. The numerical results for the wave functions, obtained by the latter methods, differed only quantitatively from those obtained by the simple HMO treatment. However, the symmetry (nodal) properties of the 'frontier' orbitals agreed among all the methods investigated here.

Method of Calculation.—The HMO method was used by diagonalisation of the appropriate topological matrices (Jacobi's method); from the eigenvectors and eigenvalues, net charges and bond orders were computed. The molecular orbitals are expressed as linear combinations $\psi_i = \sum_j c_{ij} \phi_j$, where ψ_i is the i th MO, ϕ_j the j th atomic orbital, and c_{ij} is the coefficient of the j th atom in the i th MO. In order to eliminate any dependence of the results on the parametrisation, we have chosen two sets for the Coulomb and resonance integrals of the nitrogen atom and the C=N bond. In the expressions: $\alpha_N = \alpha_C + h\beta_O$ and $\beta_{C=N} = k\beta_O$ the values of h and k

¹ R. B. Woodward and R. Hoffmann, *Angew. Chem., Internat. Edn.*, 1969, **8**, 781.

² M. Orchin and H. H. Jaffe, 'The Importance of Antibonding Orbitals,' Houghton Mifflin and Co., Boston, 1967, p. 84.

³ H. C. Longuet-Higgins and E. W. Abrahamson, *J. Amer. Chem. Soc.*, 1965, **87**, 2045.

⁴ J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, 1965, **43**, 129.

⁵ A. Pullman, 'Quantum Aspects of Heterocyclic Compounds,' The Israel Academy of Sciences and Humanities, Jerusalem, 1970, p. 30.

⁶ K. Fukui, T. Yonezawa, and H. Shingu, *J. Chem. Phys.*, 1952, **20**, 722.

⁷ O. Kikuchi, *Tetrahedron*, 1971, **27**, 2801.

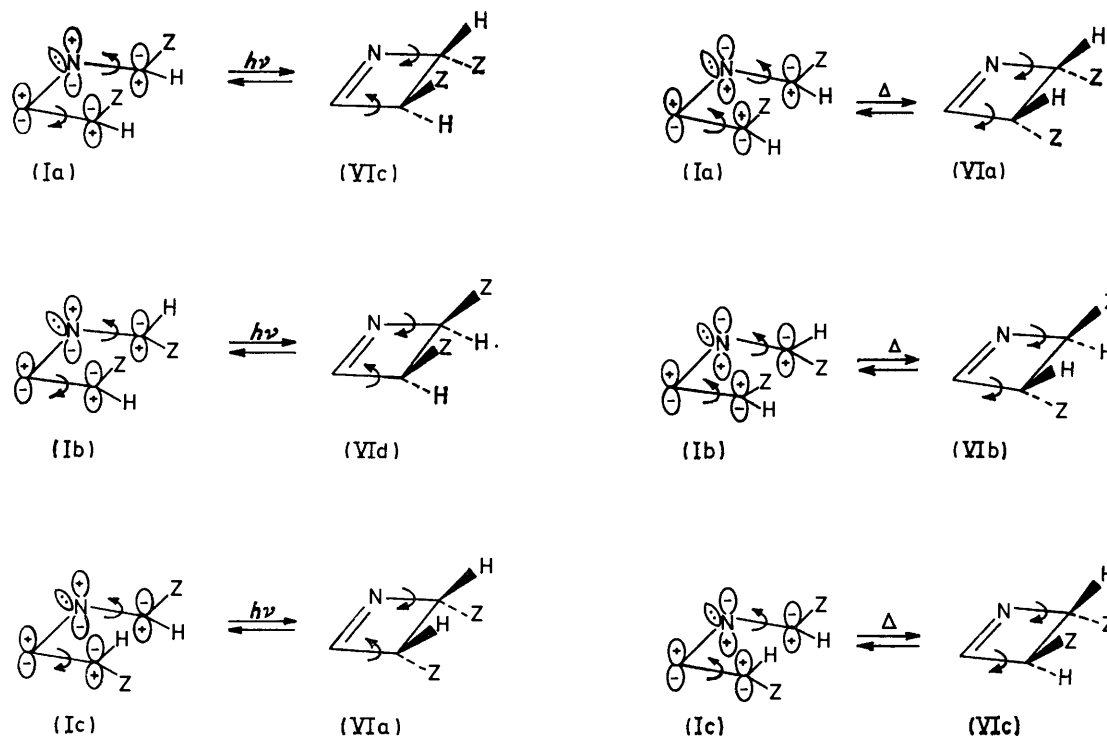
⁸ R. B. Robin, R. R. Hart, and N. A. Kuebler, *J. Amer. Chem. Soc.*, 1967, **89**, 1564.

⁹ R. Hoffman, *J. Chem. Phys.*, 1963, **39**, 1397.

TABLE I
Wave functions (HOMO and LEMO) for aza-derivatives of butadiene and hexatriene

Compound	HOMO	LEMO
Butadiene	$\psi_2 = -0.601\phi_1 - 0.372\phi_2 + 0.372\phi_3 + 0.601\phi_4$	$\psi_3 = +0.601\phi_1 - 0.372\phi_2 - 0.372\phi_3 + 0.601\phi_4$
(I)	$\psi_2 = -0.526\phi_1 - 0.353\phi_2 + 0.431\phi_3 + 0.642\phi_4$ ($\psi_2 = -0.462\phi_1 - 0.301\phi_2 + 0.485\phi_3 + 0.678\phi_4$)	$\psi_3 = -0.674\phi_1 + 0.378\phi_2 + 0.310\phi_3 - 0.553\phi_4$ ($\psi_3 = -0.712\phi_1 + 0.348\phi_2 + 0.289\phi_3 - 0.533\phi_4$) ^a
Hexatriene	$\psi_3 = +0.521\phi_1 + 0.232\phi_2 - 0.418\phi_3 - 0.418\phi_4$ + $0.232\phi_5 + 0.521\phi_6$	$\psi_4 = +0.521\phi_1 - 0.232\phi_2 - 0.418\phi_3 + 0.418\phi_4$ + $0.232\phi_5 - 0.521\phi_6$
(II)	$\psi_3 = +463\phi_1 + 0.215\phi_2 - 0.449\phi_3 - 0.424\phi_4 +$ $0.252\phi_5 + 0.542\phi_6$	$\psi_4 = +0.583\phi_1 - 0.246\phi_2 - 0.381\phi_3 + 0.407\phi_4 +$ $0.209\phi_5 - 0.495\phi_6$
(III)	($\psi_3 = +0.420\phi_1 + 0.183\phi_2 - 0.473\phi_3 - 0.429\phi_4 +$ $0.267\phi_5 + 0.557\phi_6$)	($\psi_4 = +0.616\phi_1 - 0.230\phi_2 - 0.363\phi_3 + 0.402\phi_4 +$ $0.198\phi_5 - 0.483\phi_6$)
(IV)	$\psi_3 = +0.576\phi_1 + 0.297\phi_2 - 0.422\phi_3 - 0.346\phi_4 +$ $0.244\phi_5 + 0.472\phi_6$	$\psi_4 = -0.463\phi_1 + 0.175\phi_2 + 0.396\phi_3 - 0.484\phi_4 -$ $0.213\phi_5 + 0.564\phi_6$
(V)	($\psi_3 = +0.627\phi_1 + 0.363\phi_2 - 0.379\phi_3 - 0.287\phi_4 +$ $0.250\phi_5 + 0.432\phi_6$)	($\psi_4 = -0.439\phi_1 + 0.153\phi_2 + 0.351\phi_3 - 0.519\phi_4 -$ $0.205\phi_5 + 0.590\phi_6$)
(IV)	$\psi_3 = +0.410\phi_1 + 0.220\phi_2 - 0.379\phi_3 - 0.424\phi_4 +$ $0.321\phi_5 + 0.597\phi_6$	$\psi_4 = +0.618\phi_1 - 0.222\phi_2 - 0.449\phi_3 + 0.384\phi_4 +$ $0.158\phi_5 - 0.440\phi_6$
(V)	($\psi_3 = +0.318\phi_1 + 0.178\phi_2 - 0.347\phi_3 - 0.373\phi_4 +$ $0.409\phi_5 + 0.663\phi_6$)	($\psi_4 = +0.669\phi_1 - 0.195\phi_2 - 0.470\phi_3 + 0.332\phi_4 +$ $0.131\phi_5 - 0.408\phi_6$)
(V)	$\psi_3 = +0.482\phi_1 + 0.235\phi_2 - 0.461\phi_3 - 0.461\phi_4 +$ $0.235\phi_5 + 0.482\phi_6$	$\psi_4 = -0.556\phi_1 + 0.224\phi_2 + 0.376\phi_3 - 0.376\phi_4 -$ $0.224\phi_5 + 0.556\phi_6$
(V)	($\psi_3 = +0.449\phi_1 + 0.215\phi_2 - 0.502\phi_3 - 0.502\phi_4 +$ $0.215\phi_5 + 0.449\phi_6$)	($\psi_4 = -0.575\phi_1 + 0.201\phi_2 + 0.359\phi_3 - 0.359\phi_4 -$ $0.201\phi_5 + 0.575\phi_6$)

^a Values in parentheses refer to Häfelinger's parameters.



Photochemical reaction (disrotatory)

Thermal reaction (conrotatory)

SCHEME 1 Electrocyclic reaction of 2-azabutadiene \rightleftharpoons 1-azabutene

were taken as 0.4 and 1.0 respectively, as suggested by the Pullmans,¹⁰ and as 0.8 and 1.1, as suggested by Häfelinger.¹¹ The values obtained with the last-mentioned set of parameters are given in parentheses in all Tables. The numerical calculations were performed on a CDC 6400 digital computer with use of a FORTRAN programme.

RESULTS AND DISCUSSION

Wave Functions.—Table I gives the wave functions for compounds (I)—(V) and for the corresponding hydrocarbon models, butadiene and hexatriene. It is evident

¹⁰ A. Pullman and B. Pullman, 'Quantum Biochemistry,' Interscience Publishers, New York, 1963.

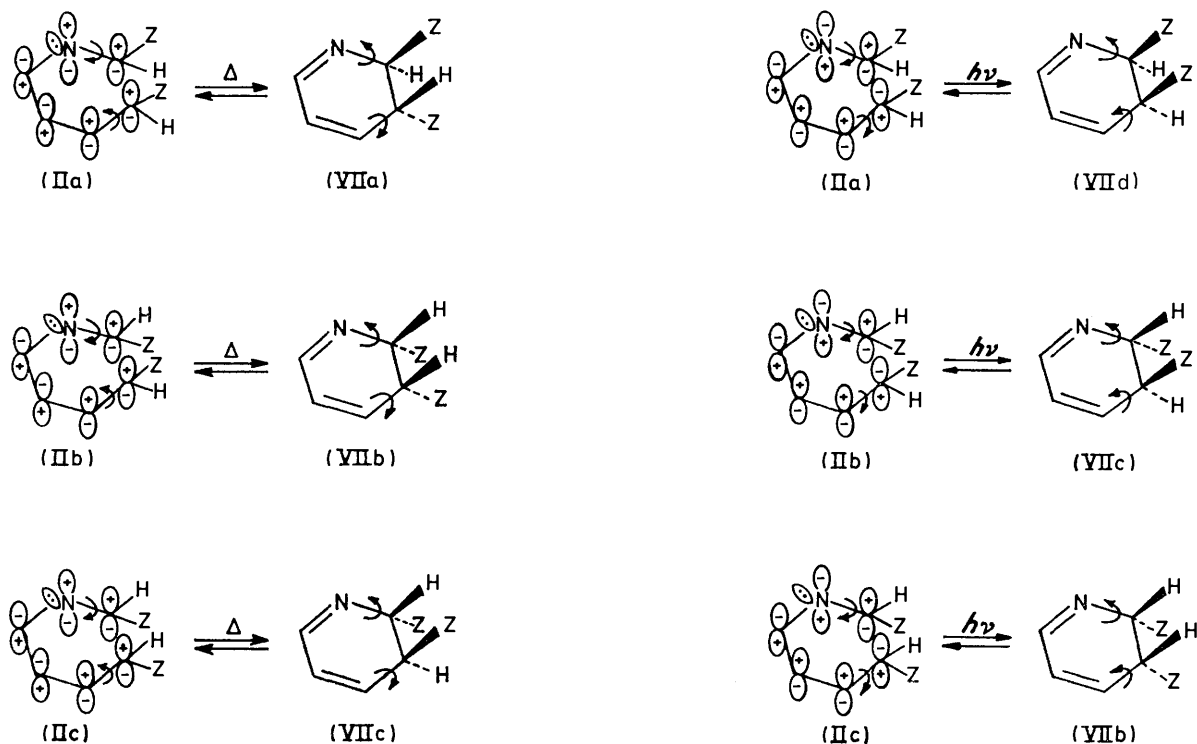
¹¹ G. Häfelinger, *Chem. Ber.*, 1970, **103**, 2941.

that the parametrisation has no influence on the nodal properties of the wave functions, and the differences observed for the numerical values of the coefficients c_{ij} of the wave functions can clearly be ignored for the purpose of qualitative comparisons. Schemes 1 and 2 show graphic representations of these wave functions and lead to the following conclusions.

2-Azabutadiene (I) is expected to react through a conrotatory mode upon thermal cyclisation, while a disrotatory mode is expected for the photochemical reaction. For 2-azahexatriene (II) the situation is

compounds (IIa) and (IIc) to undergo a thermal transformation to the *trans*-cyclic products (VIIa) and (VIIc), while isomer (IIb) would possibly be transformed into the *cis*-analogues (VIIb) and (VIId). The photochemical excitation would convert compounds (IIa) and (IIc) into the *cis*-cyclic isomers (VIId) and (VIIb), while isomer (IIb) is expected to yield the *trans*-products (VIIc) and (VIIa).

Net Charges.—Table 2 gives net charges of compounds (I)—(V) in their ground and excited states. For calculation of the ground state, it was assumed that each bonding



Thermal reaction (disrotatory)

Photochemical reaction (conrotatory)

SCHEME 2 Electrocyclic reaction of 2-azahexatriene \rightleftharpoons 2,3-dihydropyridine

reversed, *viz.*, a disrotatory path is expected for the thermal reaction and a conrotatory one for the photo-reaction. Thus, HMO predictions for compounds (I) and (II) are similar to those of their parent hydrocarbons; the nitrogen atom should cause no significant perturbation of the symmetry (nodal) properties of the wave functions of HOMO and LUMO. These functions also predict that by the thermal (conrotatory) path, 2-azabutadiene (Ia) would yield the *cis*-isomers (VIa) and (VIc), while geometric isomers (Ib) and (Ic) are expected to give the *trans*-products (VIb) and (VIc). In the photochemical transformation, 2-azabutadiene (Ia) is expected to cyclise to the *trans*-isomers (VIc) and (VIb), while isomers (Ib) and (Ic) may yield the *cis*-analogues (VIa) and (VIa).

For the 2-azahexatriene derivatives, one could expect

MO is doubly occupied, while for the excited state one of the electrons in the HOMO was transferred to the LUMO, which thus becomes a singly-occupied MO (SOMO).¹² As in Table 1, the values in parentheses refer to Häfelinger's parametrisation¹¹ (h and k values of 0.8 and 1.1 respectively). While in Table 2 the numerical values of the net charges depend somewhat on the parametrisation, the sign (whether positive or negative) is invariant to the choice of parameters. Also, in the ground state, compounds (I)—(IV) show opposite charges on the terminal carbon atoms so that the thermal (disrotatory) reaction may gain some driving force by electrostatic attraction. For compound (V), symmetry leads to equal charges of its terminal carbon atoms.

π -Bond Orders.—Table 3 gives the π -bond orders for

TABLE 2
Net charges for aza-derivatives of butadiene and hexatriene

Compound	Position	Net charges	
		Ground state	Excited state *
(I)	1	0.159 (0.275)	-0.018 (-0.018)
	2	-0.159 (-0.279)	-0.177 (-0.308)
	3	0.017 (0.034)	0.107 (0.186)
	4	-0.017 (-0.031)	0.089 (0.140)
(II)	1	0.148 (0.256)	0.022 (0.052)
	2	-0.155 (-0.272)	-0.169 (-0.291)
	3	0.022 (0.042)	0.079 (0.134)
	4	-0.011 (0.020)	0.003 (0.002)
	5	0.002 (0.004)	0.022 (0.036)
	6	-0.005 (-0.009)	0.043 (0.067)
(III)	1	-0.032 (-0.055)	0.086 (0.145)
	2	0.022 (0.042)	0.080 (0.151)
	3	-0.187 (-0.318)	-0.165 (-0.298)
	4	0.121 (0.207)	0.007 (0.020)
	5	-0.011 (-0.020)	0.002 (0.000)
	6	0.086 (0.143)	-0.009 (-0.019)
(IV)	1	0.230 (0.387)	0.016 (0.041)
	2	-0.165 (-0.287)	-0.166 (-0.293)
	3	0.144 (0.249)	0.086 (0.149)
	4	-0.196 (-0.332)	-0.163 (-0.304)
	5	0.024 (0.045)	0.102 (0.195)
	6	-0.036 (-0.062)	0.126 (0.211)
(V)	1	0.143 (0.247)	0.066 (0.118)
	2	-0.153 (-0.269)	-0.148 (-0.263)
	3	0.010 (0.022)	0.082 (0.145)
	4	0.010 (0.022)	0.082 (0.145)
	5	-0.153 (-0.269)	-0.148 (-0.263)
	6	0.143 (0.247)	0.066 (0.118)

* The values in parentheses refer to Häfelinger's parameters.

TABLE 3
 π -Bond orders (ground and excited states) for aza-derivatives of butadiene and hexatriene

Compound	Bond	Ground state	Excited state
Butadiene	1-2	0.894	0.447
	2-3	0.447	0.724
	3-4	0.394	0.447
(I)	1-2	0.882 (0.849)	0.441 (0.463) *
	2-3	0.441 (0.444)	0.711 (0.691)
	3-4	0.896 (0.893)	0.448 (0.408)
Hexatriene	1-2	0.871	0.629
	2-3	0.483	0.677
	3-4	0.785	0.435
	4-5	0.483	0.677
	5-6	0.871	0.629
(II)	1-2	0.860 (0.830)	0.617 (0.611)
	2-3	0.477 (0.478)	0.668 (0.648)
	3-4	0.787 (0.783)	0.441 (0.434)
	4-5	0.483 (0.483)	0.675 (0.678)
	5-6	0.871 (0.871)	0.631 (0.626)
(III)	1-2	0.875 (0.872)	0.623 (0.578)
	2-3	0.475 (0.474)	0.670 (0.665)
	3-4	0.770 (0.738)	0.432 (0.447)
	4-5	0.489 (0.488)	0.676 (0.667)
	5-6	0.867 (0.866)	0.632 (0.636)
(IV)	1-2	0.852 (0.813)	0.624 (0.625)
	2-3	0.485 (0.490)	0.669 (0.643)
	3-4	0.772 (0.739)	0.439 (0.453)
	4-5	0.473 (0.469)	0.669 (0.666)
	5-6	0.876 (0.875)	0.615 (0.551)
(V)	1-2	0.861 (0.832)	0.623 (0.620)
	2-3	0.476 (0.476)	0.669 (0.657)
	3-4	0.789 (0.781)	0.435 (0.400)
	4-5	0.476 (0.476)	0.669 (0.657)
	5-6	0.861 (0.832)	0.623 (0.620)

* Values in parentheses refer to Häfelinger's parameters.

ground and excited states. It is evident that parametrisation has only a minor effect on the numerical values of the bond orders. Butadiene and compound (I) show the same phenomenon when an electron is transferred from HOMO to SOMO, *viz.*, the central 2-3- σ -bond becomes 'stronger' (*i.e.*, acquires more double-bond character). In analogy to hexatriene, compounds (II)-(V) all show a similar behaviour upon passing from ground state to SOMO, *viz.*, the 1-2-, 3-4-, and 5-6-bonds became 'weaker', while the 2-3- and 4-5-bonds become 'stronger'. As expected, compound (V) shows exact symmetry of its bond orders in both ground state and SOMO.

Barton¹³ has suggested that systems isoelectronic with 1,3-cyclohexadiene, such as compounds (VII)-(X), should react photochemically through an open-chain intermediate of a hexatriene type [compounds (II)-(V)]. Beak and Miesel¹⁴ have tested this hypothesis by investigating the photochemical transformation of 2,3-dihydro-5,6-dimethylpyrazine and its 5,6-diphenyl analogue. They found that these pyrazine derivatives are transformed under irradiation in ethanol into imidazole derivatives and explained the rearrangement by an open-chain intermediate of 2,5-diazahexatriene type. Unfortunately they were unable to trap these intermediates since di-imines are rather unstable.

More recently, Padwa and his group have presented some experimental results¹⁵ which seem to be in line with the calculations presented here. They found that certain isomers of 1,3,6-triphenyl-2,5-diazahexatriene may be stable, and examined their behaviour upon thermal and photochemical activation. The stereochemistry of the products obtained by these routes seems to favour a mechanism which is dominated by the symmetry (nodal) properties of the 'frontier' orbitals. The agreement between Padwa's results and the present computations is encouraging and it seems possible that the simple HMO would be of further value for the investigation of other azapolyenes.

Conclusions.—The simple HMO method predicts that introduction of nitrogen atoms into butadiene and hexatriene should not cause any important perturbation in the course of electrocyclic reactions. Thus 2-azabutadiene (I) should react conrotatorily in a thermal reaction and disrotatorily upon photochemical excitation. The reverse is expected for the azahexatrienes (II)-(V). Similar conclusions may also be drawn from a detailed all-valence-electron calculation of the CNDO/2 or extended Hückel type. Experimental evidence partially supports these predictions.

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¹⁴ P. Beak and J. L. Miesel, *J. Amer. Chem. Soc.*, 1967, **89**, 2375.

¹⁵ A. Padwa, S. Clough, and E. Glazer, *J. Amer. Chem. Soc.*, 1970, **92**, 1778.

¹² K. Fukui, *Accounts Chem. Res.*, 1971, **4**, 57.

¹³ D. H. R. Barton, *Helv. Chim. Acta*, 1959, **42**, 2604.