X-Ray Crystallographic and Theoretical Studies of Factors Affecting the Ease of Reduction of Dioxathiadiazaheteropentalenes

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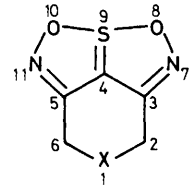
X-Ray crystal structure and molecular modelling studies have been carried out on a number of dioxathiadiazaheteropentalenes. *X*-Ray structure analysis did not yield any noticeable correlation between chemical structure and the reduction potential of the compounds studied. However, good correlation between electron affinity, calculated from molecular-orbital studies, and ease of reduction was found and this was used to predict the electrochemical properties of related molecules.

We have previously reported the electrochemical[1,2] and biochemical[3] properties of a number of herbicidal dioxathiadiazaheteropentalenes of general structure (**1**). In a similar manner to the bipyridinium compounds, paraquat (MV^{2+}) and diquat,[4] these molecules are thought to exert their phytotoxicity *via* the interruption of the photosynthetic electron-transport pathway in competition with the natural substrate ferredoxin. Optimum phytotoxic effects are found with heteropentalenes that have a reduction mid-point potential in the range *ca.* −300 to −450 mV. The acceptance of an electron from Photosystem I by these tricyclic compounds leads to the formation of an anion radical which reacts rapidly[1,3] with oxygen to give initially superoxide, $O_2^{-\bullet}$. The latter species reacts further by Fenton type chemistry to give toxic oxygen species, such as hydrogen peroxide and hydroxyl radicals. The heteropentalenes have also been found[5] to quench the emission of the excited state of $[Ru(bipy)_3]^{2+}$ at a rate faster than that observed with MV^{2+}. $[Ru(bipy)_3]^{2+}$ is very often a constituent of systems investigated in the photochemical decomposition of water.[6]



(1)

	X
(2)	CMe_2
(3)	S
(4)	SO
(5)	SO_2
(6)	CH_2

Chemical modification of the dioxathiadiazaheteropentalene (**1**) could, in principle, make possible the design of molecules showing not only enhanced biological activity, but also improved efficiency in the catalytic transfer of electrons across suitable membranes. Before any structural modifications could be carried out it was found necessary to rationalise why the reduction potential in existing molecules varies considerably (about 200 mV) on changing the group X in structure (**1**). This group appears to be 'insulated' from the expected site of reduction, that is, the dioxathiadiazabicyclic five-membered ring system. Thus in order to obtain better insight into the nature of any 'long' or 'short' range interactions between X and the site of reduction we have examined, by *X*-ray crystallography, the structures of four heteropentalenes: (**2**; X = CMe_2), (**3**; X = S), (**4**; X = SO), and (**5**; X = SO_2). We have also carried out molecular-orbital studies on these molecules with the aim of relating experimental reduction potentials to structure. These structure–activity studies have proved useful in the development of rational correlations with predictive power.

Experimental

Heteropentalene (**3**) was crystallised from ethanol. Molecules (**4**) and (**5**) were each crystallised from methanol.

Crystal Data.—Compound (**3**): $C_5H_4N_2O_2S_2$, $M = 188.2$, triclinic, $a = 7.281(2)$, $b = 8.051(2)$, $c = 12.620(3)$ Å, $\alpha = 99.13(2)$, $\beta = 95.61(2)$, $\gamma = 95.49(2)°$, $U = 722$ Å^3, space group $P\bar{1}$, $Z = 4$ (2 independent molecules), $D_c = 1.73$ g cm^{-3}, μ(Cu-K_α) = 62 cm^{-1}, $\lambda = 1.541\,78$ Å, $F(000) = 384$. Approximate crystal dimensions $0.15 \times 0.20 \times 0.20$ mm.

Compound (**4**): $C_5H_4N_2O_3S_2$, $M = 204.2$, monoclinic, $a = 7.823(2)$, $b = 9.546(3)$, $c = 10.334(2)$ Å, $\beta = 106.49(2)°$, $U = 740$ Å^3, space group $P2_1/c$, $Z = 4$, $D_c = 1.83$ g cm^{-3}, μ(Cu-K_α) = 62 cm^{-1}, $\lambda = 1.541\,78$ Å, $F(000) = 416$. Approximate crystal dimensions $0.10 \times 0.15 \times 0.33$ mm.

Compound (**5**): $C_5H_4N_2O_4S_2$, $M = 220.2$. Monoclinic, $a = 11.896(2)$, $b = 19.866(6)$, $c = 13.866(4)$ Å, $\beta = 103.94(2)°$, $U = 3\,180$ Å^3, space group $P2_1/n$, $Z = 16$ (4 independent molecules), $D_c = 1.84$ g cm^{-3}, μ(Cu-K_α) = 60 cm^{-1}, $\lambda = 1.541\,78$ Å, $F(000) = 1\,792$. Approximate crystal dimensions $0.17 \times 0.17 \times 0.43$ mm.

Data Collection and Processing.—Compound (**3**): 1 938 independent measured reflections ($\theta < 58°$), 1 742 observed [$|F_o| > 3\sigma(|F_o|)$]; compound (**4**) 997 independent measured reflections ($\theta < 58°$), 955 observed; compound (**5**) 4 285 independent measured reflections ($\theta < 58°$), 3 633 observed. All data were measured on a Nicolet R3m diffractometer with Cu-K_α radiation (graphite monochromator) using the ω-scan measuring routine. Numerical (face-indexed crystal) absorption corrections were applied to compounds (**3**) and (**4**), whereas an empirical correction, based on 434 azimuthal measurements, was applied to compound (**5**).

Structure Analysis and Refinement.—All three structures were solved by direct methods and their non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were idealised, C–H = 0.96 Å, assigned isotropic thermal parameters $U(H) = 1.2U_{eq}(C)$, and allowed to ride on their parent carbon atoms. Refinement was by block-cascade, full-matrix least-squares to give for (**3**), $R = 0.040$, $R_w = 0.044$ [$w^{-1} = \sigma^2(F) + 0.000\,74F^2$], for (**4**), $R = 0.032$, $R_w = 0.038$

Table 1. Non-hydrogen atom co-ordinates for (**3**) (× 10^4).

Atom	x	y	z
S(1)	6 795(1)	1 363(1)	2 592(1)
C(2)	5 346(5)	3 062(4)	2 857(3)
C(3)	4 547(4)	3 002(4)	3 898(3)
C(4)	5 532(4)	2 459(4)	4 757(3)
C(5)	7 289(5)	1 865(4)	4 795(3)
C(6)	8 350(5)	1 789(5)	3 837(3)
N(7)	2 907(4)	3 470(4)	4 096(3)
O(8)	2 573(4)	3 283(4)	5 102(2)
S(9)	4 473(1)	2 449(1)	5 867(1)
O(10)	6 573(4)	1 600(4)	6 411(2)
N(11)	7 856(5)	1 389(5)	5 704(3)
S(1)[a]	−2 683(1)	577(1)	9 531(1)
C(2)[a]	−1 250(5)	338(4)	8 427(3)
C(3)[a]	−272(4)	1 997(4)	8 304(2)
C(4)[a]	−1 033(4)	3 518(4)	8 580(2)
C(5)[a]	−2 708(4)	3 762(4)	9 017(2)
C(6)[a]	−3 971(4)	2 311(4)	9 210(3)
N(7)[a]	1 337(4)	2 158(4)	7 923(3)
O(8)[a]	1 870(3)	3 798(3)	7 886(2)
S(9)[a]	218(1)	5 258(1)	8 393(1)
O(10)[a]	−1 649(3)	6 380(3)	8 961(2)
N(11)[a]	−3 041(4)	5 347(4)	9 228(2)

[a] Second crystallographically independent molecule.

Table 2. Non-hydrogen atom co-ordinates for (**4**) (× 10^4).

Atom	x	y	z
O(1)	3 352(3)	1 655(2)	3 953(2)
S(1)	4 283(1)	2 632(1)	5 061(1)
C(2)	2 537(4)	3 710(3)	5 420(3)
C(3)	1 096(4)	2 802(3)	5 634(3)
C(4)	1 519(3)	1 551(3)	6 351(3)
C(5)	3 195(3)	921(3)	6 800(3)
C(6)	4 820(4)	1 583(3)	6 598(3)
N(7)	−627(3)	3 041(3)	5 141(3)
O(8)	−1 564(3)	2 033(3)	5 537(2)
S(9)	−185(1)	628(1)	6 541(1)
O(10)	1 544(3)	—683(2)	7 363(2)
N(11)	3 195(4)	−333(3)	7 331(2)

Table 3. Non-hydrogen atom co-ordinates for (**5**) (× 10^4).

Atom	x	y	z
S(1)	9 642(1)	1 950(1)	7 940(1)
O(1)	8 682(2)	1 559(1)	8 077(2)
O(2)	10 786(2)	1 674(1)	8 195(2)
C(2)	9 318(3)	2 202(2)	6 664(3)
C(3)	8 235(3)	2 610(2)	6 438(3)
C(4)	7 905(3)	2 996(2)	7 166(3)
C(5)	8 479(3)	3 063(2)	8 165(3)
C(6)	9 622(3)	2 733(2)	8 579(3)
N(7)	7 475(3)	2 606(2)	5 570(2)
O(8)	6 573(3)	3 006(2)	5 587(2)
S(9)	6 629(1)	3 378(1)	6 813(1)
O(10)	6 897(2)	3 626(1)	8 132(2)
N(11)	7 904(3)	3 395(2)	8 712(3)
S(1)[a]	2 714(1)	3 106(1)	7 285(1)
O(1)[a]	3 530(2)	3 641(1)	7 327(2)
O(2)[a]	1 494(2)	3 246(1)	7 026(2)
C(2)[a]	3 060(3)	2 692(2)	8 461(3)
C(3)[a]	4 268(3)	2 428(2)	8 651(2)
C(4)[a]	4 706(3)	2 173(2)	7 873(2)
C(5)[a]	4 177(3)	2 174(2)	6 853(2)
C(6)[a]	2 995(3)	2 472(2)	6 452(3)
N(7)[a]	5 000(3)	2 427(2)	9 524(2)
O(8)[a]	6 005(2)	2 145(1)	9 462(2)
S(9)[a]	6 044(1)	1 874(1)	8 211(1)
O(10)[a]	5 839(2)	1 719(1)	6 835(2)
N(11)[a]	4 825(3)	1 938(2)	6 281(2)
S(1)[b]	8 443(1)	578(1)	10 135(1)
O(1)[b]	7 555(2)	1 068(1)	10 110(2)
O(2)[b]	9 631(2)	789(1)	10 342(2)
C(2)[b]	8 304(3)	−67(2)	10 998(3)
C(3)[b]	7 143(3)	−393(2)	10 668(3)
C(4)[b]	6 590(3)	−451(2)	9 649(3)
C(5)[b]	6 961(3)	−195(2)	8 835(3)
C(6)[b]	8 096(3)	149(2)	8 962(3)
N(7)[b]	6 529(3)	−608(2)	11 276(2)
O(8)[b]	5 520(2)	−874(2)	10 763(2)
S(9)[b]	5 287(1)	−811(1)	9 388(1)
O(10)[b]	5 276(2)	−610(1)	8 081(2)
N(11)[b]	6 216(3)	−269(2)	7 976(2)
S(1)[c]	6 452(1)	525(1)	4 613(1)
O(1)[c]	7 241(2)	970(1)	4 299(2)
O(2)[c]	5 257(2)	712(1)	4 451(2)
C(2)[c]	7 016(3)	372(2)	5 910(3)
C(3)[c]	8 181(3)	52(2)	6 069(3)
C(4)[c]	8 444(3)	−379(2)	5 359(3)
C(5)[c]	7 753(3)	−544(2)	4 418(3)
C(6)[c]	6 552(3)	−280(2)	4 063(3)
N(7)[c]	9 025(3)	149(2)	6 856(2)
O(8)[c]	9 955(2)	−221(1)	6 804(2)
S(9)[c]	9 766(1)	−708(1)	5 659(1)
O(10)[c]	9 339(3)	−1 094(1)	4 397(2)
N(11)[c]	8 267(3)	−929(2)	3 878(3)

[a,b,c] The three other crystallographically independent molecules.

[$w^{-1} = \sigma^2F) + 0.000\ 30F^2$], and for (**5**) $R = 0.044$, $R_w = 0.046$ [$w^{-1} = \sigma^2(F) + 0.000\ 36F^2$]. Computations were carried out on an Eclipse S140 computer using the SHELXTL program system.[7]

The fractional co-ordinates of the hydrogen atoms and their isotropic thermal parameters, the bond lengths and bond angles, and the anisotropic thermal parameters of the non-hydrogen atoms have been deposited at the Cambridge Crystallographic Data Centre (CCDC).*

Computational Procedure.—The calculations were carried out using the standard MNDO parameters as implemented in the MOPAC program.[8] A standard s/p valence basis set was employed and all geometrical parameters were optimised, maintaining C_s symmetry throughout. The final optimised geometrics did not in fact correspond to true ground states, non-planar distortions leading to lower energies. Since our purpose was to compare trends in the orbital energies and geometries, we restricted ourselves only to geometries with the C_s symmetry. In several cases, the final wavefunction was decomposed further into an analysis of the σ and π contributions to the ring and into two-centre energy contributions.[8] Adiabatic electron affinities were obtained by calculating the energy of the radical anion with full optimisation of geometrical variables in C_s symmetry, using an unrestricted Hartree–Fock procedure which results in variationally exact energies and pure spin states.†

Results and Discussion

Fractional co-ordinates for the non-hydrogen atoms of compounds (**3**), (**4**), and (**5**) are given in Tables 1, 2, and 3 respectively. Table 4 compares the bond lengths of (**3**), (**4**), and

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* *Supplementary data* (see Instructions for Authors in the January issue).

† We are grateful to Dr. John McKelvey (Eastman Kodak, Rochester) for supplying one of us with a copy of the ROUHF version of MOPAC.

Table 4. Comparative bond lengths/Å, e.s.d.s in parentheses.

				(5)	
Atoms	(2)[a]	(3)	(4)		
X(1)–C(2)	1.586(17)	1.816(4)	1.830(3)	1.788(4)	1.783(4)
		1.818(4)		1.787(4)	1.787(3)
C(2)–C(3)	1.508(17)	1.492(5)	1.474(4)	1.490(5)	1.492(5)
		1.490(5)		1.494(5)	1.493(5)
C(3)–C(4)	1.410(17)	1.393(5)	1.395(4)	1.397(5)	1.401(5)
		1.400(4)		1.412(5)	1.396(5)
C(4)–C(5)	1.398(17)	1.407(5)	1.397(4)	1.396(5)	1.403(4)
		1.404(4)		1.402(5)	1.403(4)
C(5)–C(6)	1.480(17)	1.494(5)	1.487(4)	1.494(5)	1.504(4)
		1.483(4)		1.485(5)	1.490(5)
C(6)–X(1)	1.571(17)	1.810(4)	1.823(3)	1.792(4)	1.794(4)
		1.830(4)		1.794(4)	1.788(4)
C(3)–N(7)	1.296(15)	1.321(5)	1.319(4)	1.320(4)	1.309(4)
		1.312(4)		1.313(5)	1.307(4)
N(7)–O(8)	1.365(14)	1.346(5)	1.342(4)	1.340(5)	1.342(4)
		1.350(4)		1.346(4)	1.343(4)
O(8)–S(9)	1.878(8)	1.849(3)	1.845(2)	1.840(3)	1.828(3)
		1.849(3)		1.864(3)	1.828(3)
S(9)–O(10)	1.875(8)	1.849(3)	1.861(2)	1.847(3)	1.890(3)
		1.843(3)		1.853(3)	1.865(3)
O(10)–N(11)	1.351(14)	1.358(5)	1.344(4)	1.352(4)	1.338(4)
		1.351(4)		1.345(4)	1.345(4)
C(5)–N(11)	1.326(15)	1.308(5)	1.317(4)	1.315(5)	1.317(5)
		1.313(4)		1.310(4)	1.320(5)
C(4)–S(9)	1.643(9)	1.665(3)	1.655(3)	1.661(3)	1.658(3)
		1.659(3)		1.666(3)	1.661(3)
X(1)–A[b]	1.534(17)		1.496(2)	1.432(3)	1.432(3)
				1.431(3)	1.431(3)
X(1)–B[b]	1.520(17)			1.430(3)	1.436(3)
				1.435(3)	1.433(3)

[a] Values from ref. 9. [b] A=B=Me in (**2**), A=O in (**4**), A=B=O in (**5**)

Table 5. Bond angles/° for (**3**).

C(2)–S(1)–C(6)	99.6(2)	S(1)–C(2)–C(3)	110.1(3)
C(2)–C(3)–C(4)	121.2(3)	C(2)–C(3)–N(7)	124.3(3)
C(4)–C(3)–N(7)	114.5(3)	C(3)–C(4)–C(5)	128.2(3)
C(3)–C(4)–S(9)	116.1(3)	C(5)–C(4)–S(9)	115.7(3)
C(4)–C(5)–C(6)	120.3(3)	C(4)–C(5)–N(11)	115.0(3)
C(6)–C(5)–N(11)	124.8(3)	S(1)–C(6)–C(5)	111.0(2)
C(3)–N(7)–O(8)	110.7(3)	N(7)–O(8)–S(9)	113.8(2)
C(4)–S(9)–O(8)	84.8(2)	C(4)–S(9)–O(10)	85.0(1)
O(8)–S(9)–O(10)	169.9(1)	S(9)–O(10)–N(11)	113.7(2)
C(5)–N(11)–O(10)	110.6(3)	C(2)–S(1)–C(6)[a]	100.9(2)
S(1)–C(2)–C(3)[a]	111.3(2)	C(2)–C(3)–C(4)[a]	121.8(3)
C(2)–C(3)–N(7)[a]	123.5(3)	C(4)–C(3)–N(7)[a]	114.7(3)
C(3)–C(4)–C(5)[a]	128.2(3)	C(3)–C(4)–S(9)[a]	116.1(2)
C(5)–C(4)–S(9)[a]	115.7(2)	C(4)–C(5)–C(6)[a]	121.2(3)
C(4)–C(5)–N(11)[a]	114.8(3)	C(6)–C(5)–N(11)[a]	124.0(3)
S(1)–C(6)–C(5)[a]	111.4(2)	C(3)–N(7)–O(8)[a]	110.5(3)
N(7)–O(8)–S(9)[a]	113.9(2)	C(4)–S(9)–O(8)[a]	84.8(1)
C(4)–S(9)–O(10)[a]	85.1(1)	O(8)–S(9)–O(10)[a]	169.9(1)
S(9)–O(10)–N(11)[a]	113.9(2)	C(5)–N(11)–O(10)[a]	110.5(3)

[a] See Table 1.

Table 6. Bond angles/° for (**4**).

O(1)–S(1)–C(2)	106.1(1)	O(1)–S(1)–C(6)	105.5(1)
C(2)–S(1)–C(6)	97.7(1)	S(1)–C(2)–C(3)	110.0(2)
C(2)–C(3)–C(4)	120.2(2)	C(2)–C(3)–N(7)	125.2(3)
C(4)–C(3)–N(7)	114.5(3)	C(3)–C(4)–C(5)	127.1(3)
C(3)–C(4)–S(9)	116.2(2)	C(5)–C(4)–S(9)	116.3(2)
C(4)–C(5)–C(6)	122.0(2)	C(4)–C(5)–N(11)	114.8(3)
C(6)–C(5)–N(11)	123.1(2)	S(1)–C(6)–C(5)	111.1(2)
C(3)–N(7)–O(8)	110.2(3)	N(7)–O(8)–S(9)	114.2(2)
C(4)–S(9)–O(8)	84.7(1)	C(4)–S(9)–O(10)	84.7(1)
O(8)–S(9)–O(10)	168.1(1)	S(9)–O(10)–N(11)	113.6(2)
C(5)–N(11)–O(10)	110.5(2)		

(**5**) with those for (**2**) taken from the literature.[9] Tables 5, 6, and 7 give, respectively, the bond angles for (**3**), (**4**), and (**5**).

Crystals of the sulphoxide (**4**) contained only one crystallographically independent molecule whilst those of the sulphide (**3**) and the sulphone (**5**) contained two and four independent molecules, respectively. Inspection of the bond lengths (Table 4) showed that the only significant differences between the independent molecules in (**5**) are slight deviations from ideal C_s symmetry. Figures 1(*a*), (*b*), and (*c*), show perspective drawings of (**3**), (**4**), and (**5**), respectively and give the crystallographic numbering.

The dihedral angles between the two fused five-membered rings in (**3**), (**4**), and (**5**) are different. In (**3**) the two rings are essentially coplanar with dihedral angles for the two independent molecules of 0.9 and 1.4°, respectively. Oxidation of the sulphur atom, S(1), to give the sulphoxide (**4**) increases the dihedral angle to 7.2°. Further oxidation to the sulphone (**5**) reduces this dihedral angle to values of 5.2, 5.1, 5.8, and 4.0° for the four independent molecules, as expected. The non-zero value in structure (**5**) can be attributed to the asymmetric substitution of S(1), (axial/equatorial) relative to the molecular ring plane. There is, however, no correlation between the dihedral angles and the transannular C(2)–C(6) distances in these molecules.

The average C–C bond length in the five-membered rings (**2**)–(**5**) is *ca.* 1.4 Å, which is intermediate between a C–C single (1.54) and a C=C double bond (1.33 Å). This indicates that

Table 7. Bond angles/° for (**5**).

O(1)–S(1)–O(2)	120.1(2)	O(1)–S(1)–C(2)	107.1(2)
O(2)–S(1)–C(2)	108.5(2)	O(1)–S(1)–C(6)	107.4(2)
O(2)–S(1)–C(6)	109.6(2)	C(2)–S(1)–C(6)	102.8(2)
S(1)–C(2)–C(3)	109.3(3)	C(2)–C(3)–C(4)	121.8(3)
C(2)–C(3)–N(7)	123.8(4)	C(4)–C(3)–N(7)	114.3(3)
C(3)–C(4)–C(5)	127.9(3)	C(3)–C(4)–S(9)	115.7(2)
C(5)–C(4)–S(9)	116.3(3)	C(4)–C(5)–C(6)	121.4(3)
C(4)–C(5)–N(11)	115.0(3)	C(6)–C(5)–N(11)	123.4(3)
S(1)–C(6)–C(5)	108.1(2)	C(3)–N(7)–O(8)	110.9(3)
N(7)–O(8)–S(9)	113.7(2)	C(4)–S(9)–O(8)	85.2(2)
C(4)–S(9)–O(10)	84.4(2)	O(8)–S(9)–O(10)	169.0(1)
S(9)–O(10)–N(11)	114.6(2)	C(5)–N(11)–O(10)	109.6(3)
O(1)–S(1)–O(2)[a]	120.0(2)	O(1)–S(1)–C(2)[a]	107.5(1)
O(2)–S(1)–C(2)[a]	108.4(2)	O(1)–S(1)–C(6)[a]	108.5(2)
O(2)–S(1)–C(6)[a]	108.0(2)	C(2)–S(1)–C(6)[a]	103.1(2)
S(1)–C(2)–C(3)[a]	108.9(3)	C(2)–C(3)–C(4)[a]	120.8(3)
C(2)–C(3)–N(7)[a]	124.2(3)	C(4)–C(3)–N(7)[a]	115.0(3)
C(3)–C(4)–C(5)[a]	128.0(3)	C(3)–C(4)–S(9)[a]	115.0(2)
C(5)–C(4)–S(9)[a]	116.9(3)	C(4)–C(5)–C(6)[a]	121.7(3)
C(4)–C(5)–N(11)[a]	114.9(3)	C(6)–C(5)–N(11)[a]	123.3(3)
S(1)–C(6)–C(5)[a]	110.0(2)	C(3)–N(7)–O(8)[a]	110.3(3)
N(7)–O(8)–S(9)[a]	114.2(2)	C(4)–S(9)–O(8)[a]	85.4(1)
C(4)–S(9)–O(10)[a]	83.8(1)	O(8)–S(9)–O(10)[a]	168.5(1)
S(9)–O(10)–N(11)[a]	113.9(2)	C(5)–N(11)–O(10)[a]	110.3(3)
O(1)–S(1)–O(2)[b]	119.4(2)	O(1)–S(1)–C(2)[b]	108.5(2)
O(2)–S(1)–C(2)[b]	108.7(2)	O(1)–S(1)–C(6)[b]	107.0(1)
O(2)–S(1)–C(6)[b]	108.7(2)	C(2)–S(1)–C(6)[b]	103.2(2)
S(1)–C(2)–C(3)[b]	109.5(2)	C(2)–C(3)–C(4)[b]	121.0(3)
C(2)–C(3)–N(7)[b]	124.1(3)	C(4)–C(3)–N(7)[b]	114.8(3)
C(3)–C(4)–C(5)[b]	127.9(3)	C(3)–C(4)–S(9)[b]	115.9(3)
C(5)–C(4)–S(9)[b]	115.9(2)	C(4)–C(5)–C(6)[b]	121.6(3)
C(4)–C(5)–N(11)[b]	114.6(3)	C(6)–C(5)–N(11)[b]	123.7(3)
S(1)–C(6)–C(5)[b]	109.3(3)	C(3)–N(7)–O(8)[b]	110.6(3)
N(7)–O(8)–S(9)[b]	114.1(2)	C(4)–S(9)–O(8)[b]	84.6(2)
C(4)–S(9)–O(10)[b]	84.7(2)	O(8)–S(9)–O(10)[b]	168.4(1)
S(9)–O(10)–N(11)[b]	113.9(2)	C(5)–N(11)–O(10)[b]	110.8(3)
O(1)–S(1)–O(2)[c]	119.5(2)	O(1)–S(1)–C(2)[c]	107.2(2)
O(2)–S(1)–C(2)[c]	108.6(2)	O(1)–S(1)–C(6)[c]	107.8(2)
O(2)–S(1)–C(6)[c]	109.2(2)	C(2)–S(1)–C(6)[c]	103.2(2)
S(1)–C(2)–C(3)[c]	109.4(3)	C(2)–C(3)–C(4)[c]	121.0(3)
C(2)–C(3)–N(7)[c]	124.1(3)	C(4)–C(3)–N(7)[c]	115.0(3)
C(3)–C(4)–C(5)[c]	128.2(3)	C(3)–C(4)–S(9)[c]	115.1(2)
C(5)–C(4)–S(9)[c]	116.6(3)	C(4)–C(5)–C(6)[c]	121.7(3)
C(4)–C(5)–N(11)[c]	114.5(3)	C(6)–C(5)–N(11)[c]	123.7(3)
S(1)–C(6)–C(5)[c]	109.3(2)	C(3)–N(7)–O(8)[c]	110.6(3)
N(7)–O(8)–S(9)[c]	113.9(2)	C(4)–S(9)–O(8)[c]	85.4(1)
C(4)–S(9)–O(10)[c]	84.2(2)	O(8)–S(9)–O(10)[c]	169.1(1)
S(9)–O(10)–N(11)[c]	114.2(3)	C(5)–N(11)–O(10)[c]	110.3(3)

[a,b,c] As in Table 3.

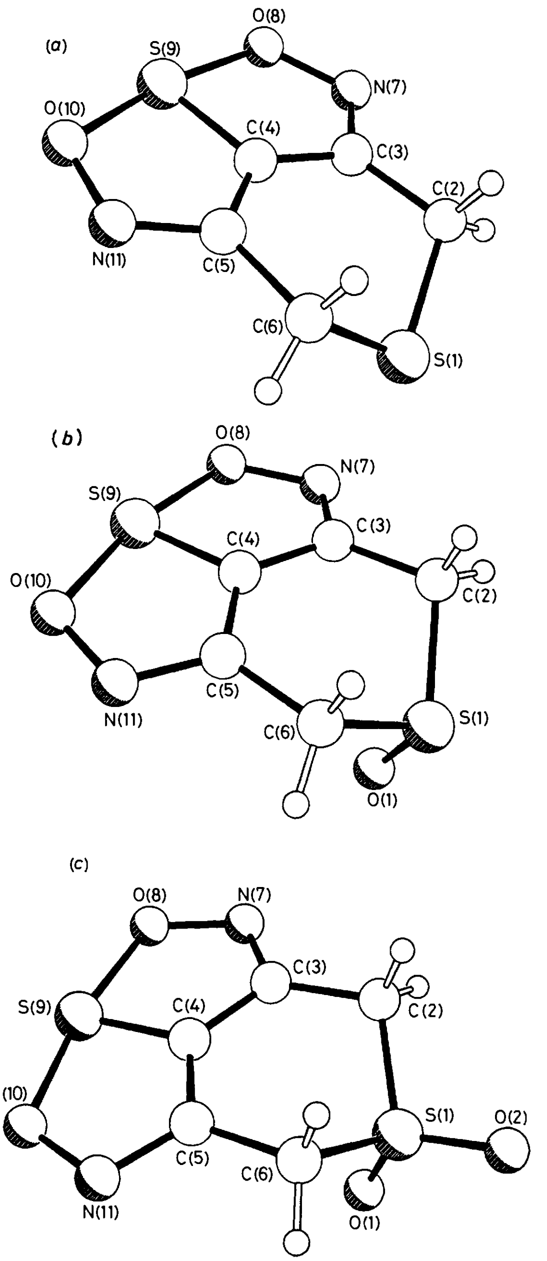


Figure 1. Representative perspective views of: (*a*) (**3**); (*b*) (**4**); and (*c*) (**5**) giving crystallographic numbering schemes.

π-delocalization is spread over the two fused five-membered rings. The other C–C bond distance between carbons in the six-membered ring and those in the heteropentalene ring system are again shorter, *ca.* 1.49 Å, than that expected for a normal fully saturated C–C single bond. This shortening is in part due to one of the atoms being an sp^2 carbon which has a smaller covalent radius than an sp^3 carbon. It may also be due to the C–C bond acquiring some double bond character in a process whereby a C–H bonding orbital interacts with the p-orbital on the adjacent sp^2 carbon. It is noticeable that the electron density on the carbon atoms C(2) and C(6) in the cyclohexyl ring system is negative and is compensated by a positive charge on the attached hydrogen atom. Using n.m.r. spectroscopy we have previously[2] shown that these hydrogen atoms are quite acidic and exchange when a solution of either (**4**) or (**5**) in [$^2H_6$]DMSO is shaken with a solution of NaOD (0.01 mol dm^{-3}).

The lack of strain appears to characterise all four heteropentalene molecules. In fact, variation of X in (**1**) does not lead to noticeable changes in the bond distances and angles in the fused ring system. For instance, S–O distances in the fused heteropentalene rings vary randomly from one molecule to another and are within the range 1.83 to 1.89 Å. Moreover, the distance between the non-bonded carbon atoms C(3) and C(5) is about 2.80 Å for all the four heteropentalenes analysed. The smaller C(2)–S(1)–C(6) angle in (**3**), (**4**), and (**5**) compared with the corresponding C(3)–C(4)–C(5) angle in (**2**), appears to be compensated by the longer C–S distances compared with the equivalent C–C distances in (**2**).

The *X*-ray structure analyses of the four heteropentalenes under study did not reveal any major differences in chemical structure that could be directly related to the reduction potential of these molecules. In particular it should be noted (Table 4) that there are no systematic changes in the C(6)–S(1) and C(2)–S(1) bond lengths in (**3**), (**4**), and (**5**) despite the different reduction potentials. This emphasises the accepted

Table 8. Calculated MNDO energies.

X	ΔH^f/kcal mol^{-1} (R)^a	ΔH^f/kcal mol^{-1} (R$^{-\cdot}$)^b	E_{LUMO}/eV	E_A/eV^d	E_{obs}/mV
CH_2	65.51	3.56	2.245	2.685	−693
S	69.80	1.47	2.502	2.962	−643
SO(*endo*)	89.90	15.29^c	2.597	3.234	−573
SO(*exo*)	90.36	15.29^c	2.743	3.254	—
SO_2	140.59	56.82	3.095	3.631	−523
NMe	88.45	25.56	2.258	2.726	—
O	43.23	−23.32	2.446	2.885	—

[a] Heat of formation of the neutral molecules (prior to reduction). [b] Heat of formation of the corresponding anion radicals. [c] Radical anions planar, with no separate *exo* and *endo* forms. [d] Adiabatic electron affinity as given by $\Delta H^f_{298}(R) - \Delta H^f_{298}(R^{-\cdot})$.

Table 9. Analysis of the wavefunction for (**3**), (**5**), and (**6**).

X	C(2)–C(3) π bond order	C(2)–C(3) two-centre energy/eV
CH_2	0.0294	−15.71
S	0.0309	−15.75
SO_2	0.0351	−15.94

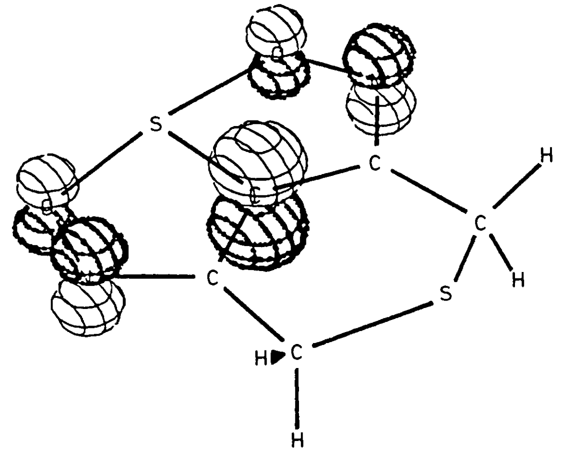


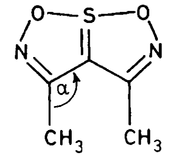
Figure 2. Calculated functional form for the lowest unoccupied molecular orbital in (**3**).

view[10] that sulphur in sulphoxides and sulphones exerts only an inductive rather than a mesomeric effect.

In order to understand some of the reasons that contribute to the ease of reduction by the heteropentalenes we carried out a detailed theoretical study of the electronic acceptor properties of molecules (**3**), (**4**), (**5**), and (**6**; X = CH_2); results are collected in Table 8.

The calculated form of the LUMO (Figure 2) shows electron density on C(1) with smaller contributions from the N–O components. This is consistent with the previous observation that the e.s.r. spectrum (X=S) is a quintet arising from coupling of the unpaired electron with two equivalent nitrogen nuclei and four equivalent hydrogen nuclei. The calculated spin density on C(1) varies only slightly with substituent X, ranging from 0.559 (X=NMe) to 0.593 (X=O).

Listed in Table 8 are the calculated LUMO energies (corresponding to vertical electron affinities) for a range of substituents (X=CH_2, S, SO, SO_2, O, and NMe), together with the adiabatic electron affinities calculated from the difference in energy between the neutral species and the radical anion, and the observed reduction potentials. The radical anions were predicted to be planar (there being no distinction between *endo* and *exo* forms for X=SO) whereas the neutral species were significantly non-planar, as observed in the *X*-ray structures. It is noteworthy that the calculations predict the *endo* isomer of the sulphoxide (**4**) to be favoured over the *exo* form, albeit by only 0.46 kcal mol^{-1}, in agreement with the *X*-ray structure [Figure 1(*b*)]. Both the calculated vertical (E_{LUMO}) (correlation coefficient $r = 0.94$) and adiabatic electron affinities (E_A) (correlation coefficient $r = 0.99$) correlate reasonably well with the observed reduction potentials (Table 8). Indeed the correlation is such that we have used this procedure to predict the reduction potentials of related and hitherto unsynthesised molecules (e.g. for X=O, E −653; X=NMe, E −682 mV). It is worth noting that whilst the absolute values of the calculated heats of formations of (**5**) are certainly too high, due to the hypervalent oxidation states of the sulphur,[11] the calculated substituent effects on both the LUMO energy and the difference in energy between the neutral species and the radical anion are more reliably predicted. Since the subsitutent X does not contribute to the LUMO orbital, its effect must be transmitted *via* the σ framework. The mechanism for this could be either inductive, or due in some way to a change in ring strain as a consequence of the changing size of the substituent X. From the previous crystallographic discussion no significant ring strain was apparent in molecules (**2**)–(**5**). The possibility of strain was also investigated by calculating the LUMO energy of model molecule (**7**) as a function of the angle α. The results (α, E_{LUMO}: 115°, −2.356; 145°, −2.138) confirm that ring strain has little effect on the LUMO energies. The inductive effect was also analysed by decomposing the MNDO wavefunction into σ and π contributions[1] and into two-centre energy terms (Table 9). Increasing the electronegativity of the substituent X increases both the C(2)–C(3) π bond order and the two-centre energy of the C(2)–C(3) bonds, suggesting that in part, the substituent effect is transmitted by increasing the hyperconjugation of the α ring substituents.



(**7**)

In conclusion, whereas the crystallographic analyses show no noticeable correlation between reduction potential and structural parameters, the theoretical study has revealed a distinctive correlation between electron affinity and ease of reduction. This approach was used to predict the electrochemical properties of related heteropentalenes.

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