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MESOMERIC BETAINE DERIVATIVES OF HETEROPENTALENES

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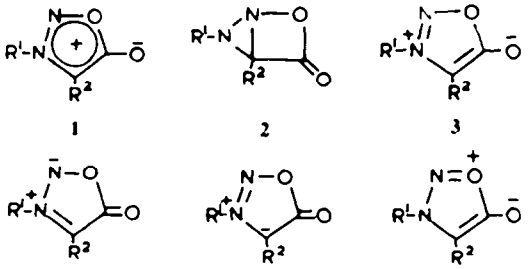
I. INTRODUCTION

When plans were made for the creation of the Universe neither pencil nor paper were used by the architect. Subsequently the antics of Earthlings in trying to make graphic copies of these cosmogonical blueprints must have caused great amusement in higher circles. In general organic chemists have been very successful in representing molecules by classical covalent structures depicting localised σ- and π-bonds but occasionally a group of delinquent molecules are found which refuse to conform to the man-made rules. A classic case is the sydnones (1);[1] first prepared in 1935 by Earl and Mackney at the University of Sydney. The original proposal of a bicyclic β-lactone structure (2)[1,2] for these compounds was later dismissed as unsatisfactory[3,4] but no alternative covalent structure was obvious. The problem was resolved in 1946 when Baker and Ollis[3,5] recognised that the sydnones (1) belong to a large family of 5-membered heterocycles which cannot be represented satisfactorily by any one covalent or polar structure. Their true structure (in valence bond terminology) is a resonance hybrid of many dipolar canonical forms (e.g. 3–6) and it was proposed that these molecules should be described as meso-ionic and represented by structures of the type 1.[3]



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4 5 6

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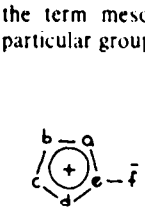
Since the introduction of the term, many new meso-ionic systems have been prepared and because of their interesting chemistry and their pharmacological activity this continues to be an active and rewarding area of research. A recent review[6] has surveyed the chemistry of meso-ionic compounds and a detailed discussion of the structure and representation of meso-ionic heterocycles is included there.[6]

In the quarter of a century which has passed since the term meso-ionic was coined, rapid progress has been made in heterocyclic chemistry and many novel and varied structural types have been reported. This has resulted in a broader interpretation of the definition of meso-ionic. 5-, 6- and 7-Membered heterocycles and bicyclic heterocycles have been described as meso-ionic and the term has found such liberal usage that its value could be questioned. In order to retain the usefulness of the term, Ollis and Ramsden,[6] in their review of meso-ionic compounds, have strongly recommended that the description meso-ionic should be restricted to 5-membered heterocycles of the general type **7**, and they have modified the definition accordingly. Thus, according to the revised definition,[6] the term meso-ionic refers to two general types of 5-membered heterocycle (type A and type B) and the description of a molecule as meso-ionic immediately and specifically classifies its structure and bonding. Even with this restriction, the definition still embraces over two hundred classes of heterocycle.

This new definition does exclude some structural types which have previously been described as meso-ionic. It has been proposed[6] that these molecules should now be described and represented as *mesomeric betaines*. Examples of molecules of this type include the 3-pyridiniumolates (**8**),[7] the pyrazinium-2,6-diolates (**9**),[8] the triazaphenalenes (**10**),[9-14] the pyrazolo[1,2-*a*]pyrazoles (**11**) and the thieno[3,4-*c*]pyrazoles (**12**). It should be emphasised that this proposed division does not imply any fundamental difference in bonding characteristics; the term meso-ionic is simply a generic name for a particular group of mesomeric betaines.



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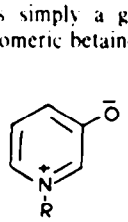

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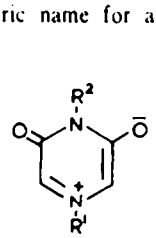

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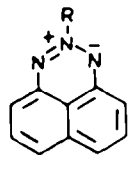

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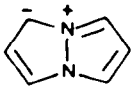

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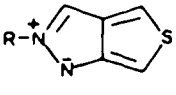

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13 14

Compared to meso-ionic compounds (**7**),[6] other mesomeric betaines (e.g. **8**–**11**) have received little attention. Recently, the interesting chemical properties of these molecules have been recognised and a variety of mesomeric betaines have undergone detailed and timely study.[7] Heteropentalene derivatives, exemplified by compounds **11** and **12**, are one such class of bicyclic heterocycle in which interest is growing. These molecules (e.g. **11** and **12**) are isoelectronic with the pentalenyl dianion (**13**) and show stability associated with heteroaromatic species as well as participating in useful 1,3-dipolar cycloaddition reactions. The purpose of this Report is to provide a comprehensive survey of their chemistry in the hope of stimulating further studies of these interesting molecules. The literature available to the author up to May 1976 has been covered.

Before embarking on a discussion of the structure and chemistry of mesomeric betaine derivatives of the heteropentalenes, their relationship to the pentalenyl dianion (**13**) and other isoelectronic species will be discussed.

II. HETERODERIVATIVES OF THE PENTALENYL DIANION

Molecules and ions which are isoelectronic with the pentalenyl dianion (**13**) constitute a large, but relatively unknown, family of heteroaromatic species. They are related to the pentalenyl dianion (**13**) in the same way that pyrrole, imidazole and similar 5-membered heterocycles are related to the aromatic cyclopentadienyl anion and are described as heteroaromatic on the understanding that the pentalenyl dianion (**13**) is an aromatic species. The stability of **13** has certainly been demonstrated by its preparation (**14** → **13**) and isolation as dilithium pentalenide[15,16] and, in spite of modern dissatisfaction with the term, it is reasonably described as aromatic in that: (a) its inherent stability is attributable to cyclic delocalisation of the annular π-electrons;[17] (b) all the π-electrons are accommodated in bonding (or non-bonding) molecular orbitals;[18] (c) the ^{1}H-NMR spectrum shows evidence of a diamagnetic ring current.[19] Furthermore, one might intuitively expect the pentalenyl dianion (**13**) to be aromatic since it is related to the cyclopentadiene anion in the same way that naphthalene is related to benzene. More naïvely one might argue that it is a 10π-electron system obeying Hückel's $4n + 2$ rule.

Heterocyclic systems isoelectronic with **13** can be subdivided into: (a) monoanions; (b) neutral molecules and (c) monocations and can be regarded as being derived by substitution of one, two and three hetero-lonepairs into the pentalenyl dianion π-system. This Report is particularly concerned with those members of the second category (neutral molecules) which cannot be represented by uncharged covalent structures and which are now described as mesomeric betaines. Before discussing these derivatives, the three heteroaromatic structural types defined above will be briefly exemplified by known derivatives.

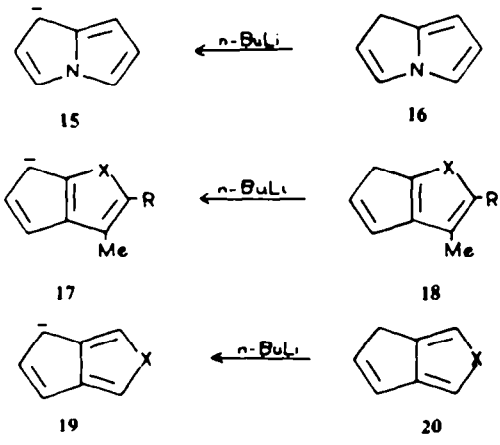
(A) *Monoanions*

The simplest heterocyclic system isoelectronic with the pentalenyl dianion (**13**) is the 4-azapentalenyl anion (**15**) derived by replacement of one of the bridgehead C atoms by a quaternary nitrogen. The chemical neologists have provided the term *azonialog* to describe aromatic nitrogen heterocycles having this relationship to a carbocycle.[20]

The preparation of the anion **15** has been reported by Okamura and Katz[21] who treated 3H-pyrrolizine (**16**) with n-butyllithium. Lithium azapentalenide can be precipitated from the cold reaction mixture; in deoxy-

genated THF solution it is stable for several months. Sodium and potassium azapentalenides were also generated and their spectral properties are consistent with the proposed ionic character. The generation of the lithium salt of a benzo derivative has also been reported.[22]

Two other types of monoanion derived from the pentalenyl dianion (13) can be envisaged by insertion of a heteroatom in either the 1- or 2-position of the carbon skeleton. Examples of both these types (17; X = NMe, R = H or Me)[23,24] and (19; X = O, NMe, S)[25-27] have been prepared by deprotonation of the appropriate methylene derivatives (18 and 20).

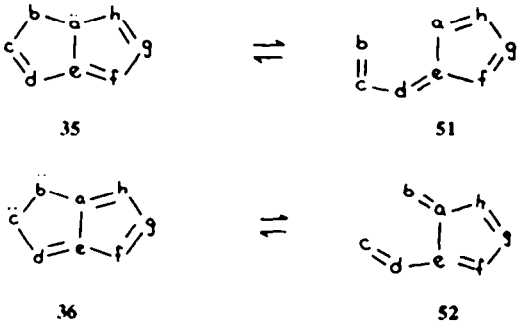


15 16 17 18 19 20

(B) *Neutral molecules*

Ten general types of heterocyclic pentalene associated with ten π-electrons can be depicted (Fig. 1; 21–30) in which a, b, c, d, e, f, g and h represent suitably substituted carbon or heteroatoms. The superscripts (see 21–30) indicate the origin of the ten π-electrons and development of the representations (21–30) gives the corresponding constitutional formulae (31–40).

These ten generalised heterocyclic types (31–40), illustrated by the known examples (41–50), demonstrate the limitations of representing delocalised aromatic systems by localised π-bonds. Six of these general types are satisfactorily represented by covalent structures. Thus, compounds 41,[28] 42,[29] 43[30] and 44[31] are acceptably represented by their covalent formulae. Similarly, compounds 45[32] and 46,[33] corresponding to the general formulae 35 and 36, present no problems in their pictorial representation. Here it should be noted, however, that because of the possibility of valence tautomerism (35⇌51), and (36⇌52), favouring the monocyclic tautomer, compounds with the general structures 35 or 36 should be formulated with caution.



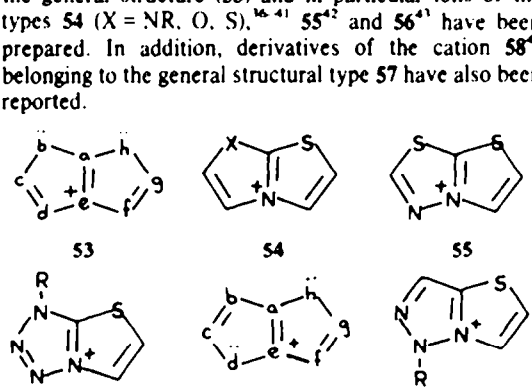
35 51 36 52

The four remaining general structural types (37–40) cannot be represented by uncharged covalent structures. Only mesomeric betaine structures can be written and the choice of any single dipolar canonical form to represent these molecules is arbitrary and may be misleading. Their true structure is a resonance hybrid of several dipolar structures and their description as mesomeric betaines seems appropriate and reasonable. The terms pseudoazulene[11] and nonclassical molecule[34] have also been used to describe some molecules of this type 37–40. The description pseudoazulene is not recommended since the isoelectronic relationship of these molecules to azulene does not have special significance. The term nonclassical has been used in relation to the possibility that, in some sulphur containing species, the participation of *d*-orbitals may be important in the bonding;[34] this aspect will be discussed in a later section. Sometimes, nitrogen derivatives of the type 37 have been referred to as polyazapentalenes[35] and this apt description provides a useful alternative name; particularly to authors trying to avoid repetitive nomenclature.

The mesomeric betaines of general structure (37–40) are the subject of this Report and the four discrete types will be referred to as type A (37), type B (38), type C (39) and type D (40).

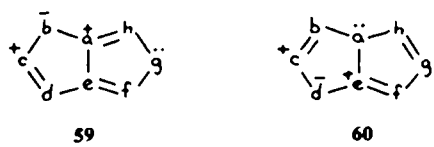
(C) *Monocations*

In principle seventeen distinct cationic structural types having a pentalene skeleton associated with ten π-electrons are possible. Since nothing is known about most of these types, they will not be systematically discussed here. Most of the known cations in this category have the general structure (53) and in particular ions of the types 54 (X = NR, O, S),[36-41] 55[42] and 56[43] have been prepared. In addition, derivatives of the cation 58[44] belonging to the general structural type 57 have also been reported.



53 54 55 56 57 58

Of the unknown cations, two general types are of special interest, namely 59 and 60. Examination of these cationic structures reveals that they can only be represented by tripolar structures and several of these structures are required to describe the cation. In fact these cations are associated with the same representational problems as the previously described mesomeric betaines (37–40). Furthermore, consideration of the electronic structure of 59 and 60 suggests that they might react as 1,3-dipoles with electron rich 1,3-dipolarophiles. The preparation of derivatives of these unknown structural types 59 and 60 would seem worthwhile.



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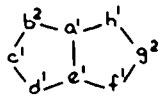

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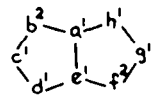

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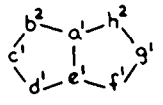

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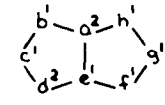

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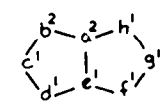

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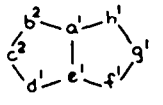

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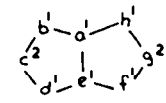

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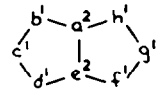

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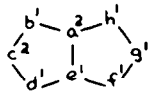

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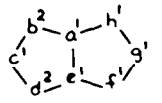

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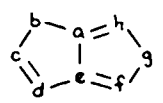

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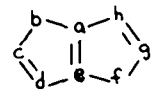

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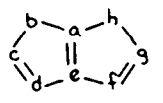

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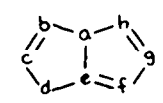

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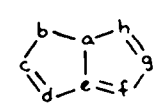

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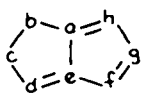

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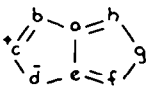

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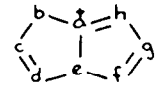

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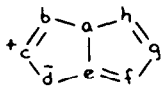

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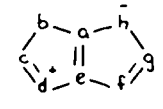

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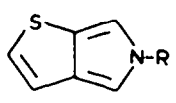

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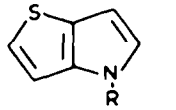

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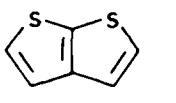

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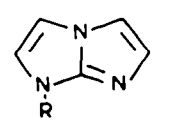

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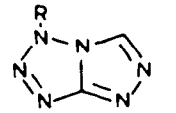

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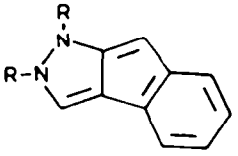

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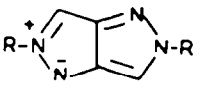

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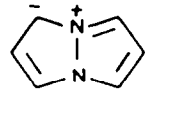

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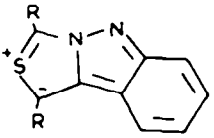

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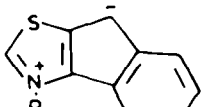

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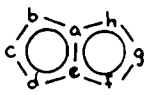
Fig. 1. Ten general types of bicyclic heterocycles (31–40), with examples.

III. THE REPRESENTATION OF HETEROPENTALENE MESOMERIC BETAINES

Since no single structure uniquely describes the bonding of the mesomeric betaines (**37–40**), the structural representation of these bicyclic heterocycles is not straightforward. The use of several canonical forms is often inconvenient and a single general representation for these structural types is clearly desirable.

Large, full circles (**61**) indicative of aromatic sextets have been employed[34] to represent these molecules but this method of representing polycyclic aromatic compounds is not in accord with the general policy of The Chemical Society and the disadvantages of this type of symbolism have been discussed.[45] In the case of unsymmetrical molecules, where a degree of polarisation might be expected, positive and negative signs have been included in the structure **62**.[33] Other methods of depicting the delocalised π-system have involved the use of broken lines, (**63**[46] and **64**),[47] and full lines (**65**).[48]



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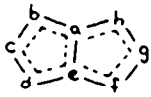

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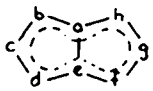

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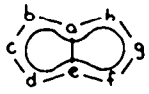

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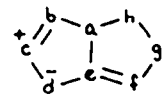
The introduction of special symbols to represent molecules inevitably results in misuse and misunderstanding. A special general formula **7** has been used for meso-ionic compounds and arguments for the continuation of the use of this formula for meso-ionic molecules have been presented.[6] However, we do not feel that the use of the special formulae (**61–65**), or the introduction of any other symbolism to represent the mesomeric betaines (**37–40**) is desirable or necessary.

We recommend that the mesomeric heteropentalene betaines (**37–40**) be generally represented by a single dipolar structure, chosen so that it is in satisfactory agreement with the observed physical and chemical properties. This proposal is in accord with the current practice of several groups of research workers in this field. If this recommendation is accepted, we propose that the type A and type B mesomeric betaines be represented by the two discrete 1,3-dipolar structures (**66** and **67**). The representations **66** and **67** have the immediate appeal of clearly distinguishing between type A and type B derivatives. Furthermore, this is an excellent representation for rationalising the 1,3-dipolar cycloaddition reactions in which many representatives of these systems participate (Section VIII, C). Due to the topology of the molecular framework the contribution of other canonical forms is implicit and this is emphasised by the description *mesomeric* betaine. The representations **66** and **67** for the type A and type B systems will be used throughout this review. The possibility of representing some sulphur derivatives belonging to type A by covalent structures involving tetracovalent sulphur (e.g. **68**) is discussed in a later section (Section VIII, B, c): in order to employ a consistent representation of type A mesomeric betaines (**66**) we have not used structures of the type **68** in the discussion of their chemistry but



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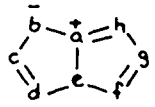

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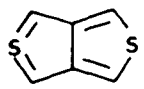


68

this does not imply that we do not recognise that *d*-orbitals are involved in the bonding.

Little is known about the structure and reactions of type C and type D mesomeric heteropentalene betaines and a discussion of their representation ought to wait until their chemistry has received more attention. We have represented these molecules by reasonable dipolar structures.

It is to be admitted that the structures (**37–40**) do not portray the aromatic character of these species—but neither do the usual structures of, for example, benzene and thiophene. In fact the usefulness of employing the overused and vague description aromatic to describe these systems (**37–40**) is questionable. Perhaps they are best regarded as stable heterocycles enjoying a favourable, cyclic conjugated π-electron system.

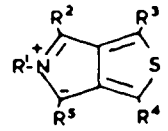
In the following sections the chemistry of the type A, B, C and D heteropentalene mesomeric betaines is discussed. Having examined their chemistry in some detail, the final sections of the Report are devoted to a discussion and comparison of general aspects of their structure, bonding and reactivity.

IV. HETEROPENTALENE MESOMERIC BETAINES OF TYPE A

If the atoms or groups a, b, c, d, e, f, g and h in the general formula **37** (Table 1) are selected from suitably substituted C, N, O and S atoms, it can be shown that 51 structural types are possible. So far, derivatives of ten of these systems **69**, **85**, **89**, **107**, **117**, **139**, **146**, **153**, **156**, **159** (Table 1) have been prepared and their chemistry is described below in the order given in Table 1. Extension of the general formula **37** to selenium provides a further 37 structural possibilities of which two representatives **158**, **163** (Table 1) are known.

(A) *Thieno*[3,4-c]*pyrroles* (**69**)

The bright red, crystalline tetraphenyl derivatives of the thieno[3,4-*c*]pyrroles (**69**; R^1 = Me or Ph, $R^2 = R^3 = R^4 = R^5$ = Ph) have been prepared in good yield by treatment of 3,4-dibenzoylpyrroles (**70**) with phosphorus pentasulphide followed by alkaline hydrolysis of an intermediate gum.[49,50] This synthesis is not suitable for the preparation of unsubstituted derivatives (**69**; R^1 = Me or Ph, $R^2 = R^3 = R^4$ = Ph, R^5 = H) where only the dithiobenzoylpyrroles (**71**; R = Me or Ph) were isolated.[51] The pyrrole precursors (**70**) are prepared by the condensation of primary amines with tetrabenzoylethane (**72**)[49,50] or more conveniently by the 1,3-dipolar cycloaddition of dibenzoylacetylene to a meso-ionic 1,3-oxazol-5-one (**73**).[51,52]



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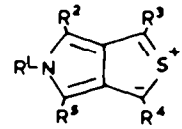

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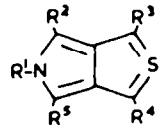
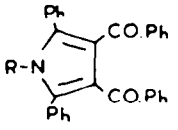


69c



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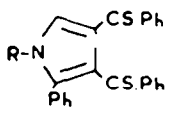

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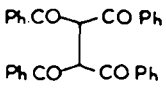

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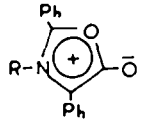

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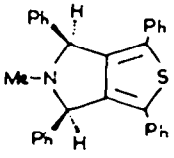
These thieno[3,4-*c*]pyrroles (**69**) can be regarded as resonance hybrids of the azomethine ylide (**69a**) and the thiocarbonyl ylide (**69b**) structures. The interesting possibility that the ylene or nonclassical structure (**69c**), involving the participation of sulphur *d*-orbitals, makes an important contribution to the bonding has also been proposed.[34]

Although crystalline samples are quite stable, the thienopyrroles (**69**) are rather unstable in solution being sensitive to light and air. Solubility in non-polar solvents such as hexane or benzene is low.[50]

The N-methyl derivative (**69**; R^1 = Me, $R^2 = R^3 = R^4 = R^5$ = Ph) is hydrogenated in the presence of Pd catalyst giving a single colourless, crystalline product to which the *cis*-dihydropyrrole structure (**74**) has been assigned.[50] The N-phenyl derivative (**69**; R^1 = Ph, $R^2 = R^3 = R^4 = R^5$ = Ph) is easily oxidised (peracetic acid) giving a mixture of the thiophene diketone (**75**) and its mono-N-phenylimine (**76**). This imine (**76**) is slowly converted to the diketone (**75**) by acid hydrolysis.[50]

The 1,3-dipolar cycloaddition reactions of the thieno[3,4-*c*]pyrroles (**69**) with olefinic 1,3-dipolarophiles are particularly interesting since they behave either as azomethine ylides (**69a**) or thiocarbonyl ylides (**69b**) depending upon the reaction conditions. 5 - Methyl - 1,3,4,6 - tetraphenylthieno[3,4-*c*]pyrrole (**69**; R^1 = Me, $R^2 = R^3 = R^4 = R^5$ = Ph) reacted rapidly with fumaronitrile in boiling benzene solution (80°) giving the primary 1:1 adduct **77** (63%) which corresponds to addition across the azomethine ylide fragment.[51] When the higher boiling solvent toluene (110°) was used, together with a longer reaction time, addition took place across the thiocarbonyl ylide giving the isomeric adduct **78** (67%) together with a small yield of the isoindole **79** (5%).[51] The even higher temperature of boiling xylene (140°) resulted in a substantial increase in the yield of the isoindole **79** (53%) and a correspondingly lower yield of the adduct **78** (5%).[51] Presumably the isoindole **79** is formed by the thermal elimination of hydrogen sulphide from this adduct **78**. The adducts **77** and **78** have similar but distinct physical and spectroscopic properties. However, whereas compound **78** is quite stable and easily recrystallised, the isomer **77** in warm solvent rapidly undergoes a retro-cycloaddition (**77** → **69**).[51] In boiling xylene the latter adduct **77** gives the isoindole **79** (60%) presumably via the sequence **77** → **78** → **79**. This mechanistic proposal is supported by the isolation of trace amounts of the adduct (**78**) from the reaction mixture.[51] The temperature dependence of the mode of 1,3-dipolar cycloaddition to the thienopyrroles (**69**) is rationalised by the supposition that addition to the azomethine ylide (**69** → **77**) is kinetically controlled whereas addition to the thiocarbonyl ylide (**69** → **78**) is thermodynamically controlled.[51]



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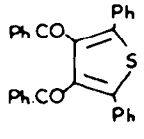

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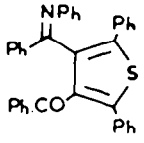

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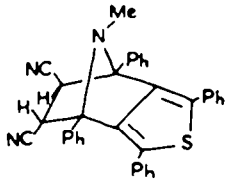

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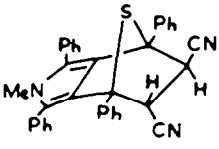

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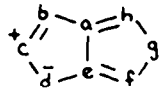
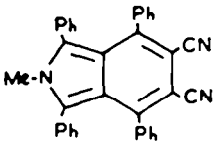
Table 1. Known mesomeric heteropentalenes of type A (37)



Parent system	Heterocycle	Atom or group[a]							
		a	b	c	d	e	f	g	h
Thieno[3,4-*c*]pyrroles	(69)	C	CR	NR	CR	C	CR	S	CR
Thieno[3,4-*c*]furans	(85)	C	CR	O	CR	C	CR	S	CR
Thieno[3,4-*c*]thiophenes	(89)	C	CR	S	CR	C	CR	S	CR
Thieno[3,4-*c*]pyrazoles	(107)	C	CR	NR	N	C	CR	S	CR
Pyrazolo[4,3-*c*]pyrazoles	(117)	C	CR	NR	N	C	CR	NR	N
Thieno[3,4-*c*]-1,2,5-thiadiazoles	(139)	C	N	S	N	C	CR	S	CR
1,2,3-Triazolo[4,5-*d*]-1,2,3-triazoles	(146)	C	N	NR	N	C	N	NR	N
1,2,3-Triazolo[4,5-*c*]-1,2,5-oxadiazoles	(153)	C	N	NR	N	C	N	O	N
1,2,3-Triazolo[4,5-*c*]-1,2,5-thiadiazoles	(156)	C	N	NR	N	C	N	S	N
1,2,3-Triazolo[4,5-*c*]-1,2,5-selenadiazoles	(158)	C	N	NR	N	C	N	Se	N
1,2,5-Thiadiazolo[3,4-*c*]-1,2,5-thiadiazole	(159)	C	N	S	N	C	N	S	N
1,2,5-Selenadiazolo[3,4-*c*]-1,2,5-thiadiazole	(163)	C	N	Se	N	C	N	S	N

[a] The groupings c and g each contribute 2 electrons to the π-electron system of the heterocycle; a, b, d, e, f and h each contribute 1 electron.



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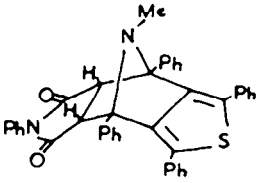

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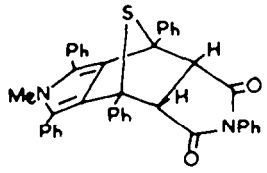

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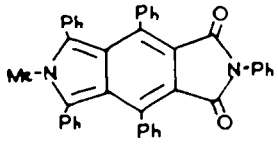
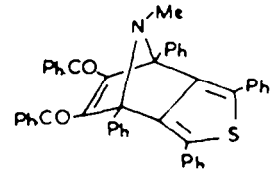


82

Similar temperature control of products was observed with acrylonitrile,[51] ethyl acrylate[51] and N-phenylmaleimide.[50,51] For example, compound **69** (R^1 = Me, R^2 = R^3 = R^4 = R^5 = Ph) reacted with N-phenylmaleimide to give the adduct **80** (68%) in boiling benzene (80°),[50,51] the isomeric adduct **81** (73%) in boiling xylene (140°)[51] and the isoindole **82** (74%) plus a low yield of adduct **81** in *o*-dichlorobenzene (180°).[50] The same compound failed to react with dimethyl fumarate, dimethyl maleate, norbornene, diphenylcyclopropenone, phenyl isocyanate or phenyl isothiocyanate.[51]

With acetylenic dipolarophiles,[50,51] only addition across the azomethine ylide portion of the thieno[3,4-*c*]pyrroles (**69**) has been observed. Thus, with dibenzoylacetylene in either boiling benzene,[51] toluene[50] or xylene,[51] the N-Me derivative **69** (R^1 = Me, R^2 = R^3 = R^4 = R^5 = Ph) gives only the adduct **83**. An apparent discrepancy in the m.p.[50,52] of this thieno[3,4-*c*]pyrrole (**69**; R^1 = Me, R^2 = R^3 = R^4 = R^5 = Ph) has been rectified;[50,51] a similar discrepancy in the m.p. of the cycloadduct **83**, (146–148°)[50] and (247–249°)[51] has now arisen! Oxidation of the cycloadduct (**83**) with *m*-chloroperbenzoic acid gives 5,6 - dibenzoyl - 1,3,4,7 - tetraphenyl - isothianaphthene (**84**), almost certainly via an N-oxide intermediate.[50] Dimethyl acetylenedicarboxylate underwent similar cycloadditions with the N-methyl and N-phenyl thieno[3,4-*c*]pyrroles (**69**; R^1 = Me and Ph, R^2 = R^3 = R^4 = R^5 = Ph).[50]



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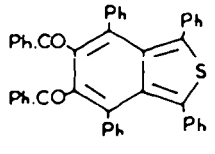

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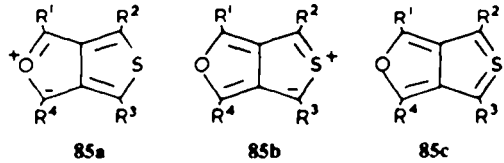
It is interesting to note that the successful synthesis of the thieno[3,4-*c*]pyrrole system (**69**) was reported soon after a molecular orbital study[53] had predicted that this system (**69**) would be very unstable. The value of pessimistic predictions by theoreticians should not be underestimated; they are a great stimulus to organic chemists.[54]

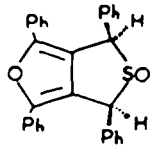
(B) *Thieno*[3,4-*c*]*furans* (**85**)

Thieno[3,4-*c*]furans (**85**) have not been isolated but evidence for the transient generation of the tetraphenyl derivative (**85**; R^1 = R^2 = R^3 = R^4 = Ph) has been



85a 85b 85c

provided by *in situ* trapping.[49,50] Dehydration of the sulphoxide (**86**) with acetic anhydride in the presence of dimethyl acetylenedicarboxylate gave a 68% yield of the cycloadduct (**87**). The structure of this adduct (**87**), formed by 1,3-dipolar cycloaddition of the acetylene to the carbonyl ylide portion of the thienofuran (**85**), was firmly established by its deoxygenation to the isothianaphthene (**88**) using triethyl phosphite. The alternative possibility that the adduct is formed by an initial Diels–Alder reaction of the sulphoxide (**86**) followed by dehydration was eliminated.[50]



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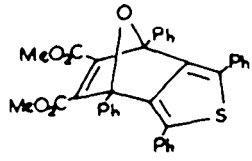

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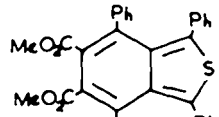
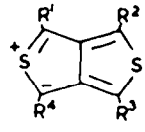
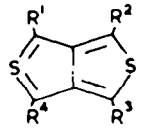


88

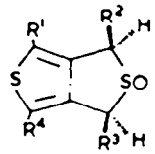
(C) *Thieno*[3,4-*c*]*thiophenes* (**89**)



89a



89b



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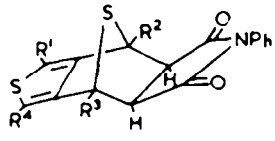

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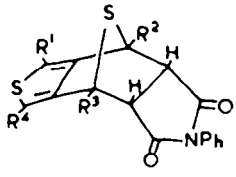


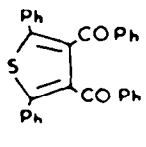
92

Pummerer dehydration[55] of the sulphoxides (**90**), obtained by periodate oxidation of the corresponding sulphides, gives thieno[3,4-*c*]thiophenes (**89**).[56–59] The 1,3-dimethyl derivative (**89**; R^1 = R^4 = Me, R^2 = R^3 = H) and the 1,3-dicarbomethoxy derivative (**89**; R^1 = R^4 = CO_2Me, R^2 = R^3 = H) are too unstable to be isolated but can be trapped *in situ* by N-phenylmaleimide giving a mixture of the *exo* and *endo* 1,3-dipolar cycloadducts **91** and **92** (R^1 = R^4 = H, R^2 = R^3 = Me) and **91** and **92** (R^1 = R^4 = CO_2Me, R^2 = R^3 = H) respectively.[57,59] The tetraphenylthieno[3,4-*c*]thiophene (**89**; R^1 = R^2 = R^3 = R^4 = Ph) is more stable and can be isolated in 87% yield as glistening, purple needles, m.p. 257–258°.[56,58] This derivative (**89**; R^1 = R^2 = R^3 = R^4 = Ph) also undergoes a 1,3-dipolar cycloaddition with N-phenylmaleimide giving

a mixture of the *exo* adduct **91** ($R^1 = R^2 = R^3 = R^4 = Ph$; 22%), m.p. 274–275°, and the *endo* adduct **92** ($R^1 = R^2 = R^3 = R^4 = Ph$; 66%), m.p. 311–312°.[56] These cycloadditions are reversed at the melting points of the adducts.

Convenient alternative routes to tetraphenylthieno[3,4-*c*]thiophene (**89**, $R^1 = R^2 = R^3 = R^4 = Ph$) involve treatment of either 3,4-dibenzoyl-2,5-diphenylthiophene (**93**)[51,60] or tetrabenzoylethane (**94**)[54] with phosphorus pentasulphide in pyridine at reflux temperature. The conditions for these transformations (**93** or **94** → **89**) are critical. When pyridine is replaced by xylene as solvent both compounds (**93** and **94**) give the 1,3-dihydro derivative (**95**).[56] The formation of this product (**95**) probably takes place via tetraphenylthieno[3,4-*c*]thiophene (**89**, $R^1 = R^2 = R^3 = R^4 = Ph$) which can also be converted to the 1,3-dihydro derivative (**89** → **95**; $R^1 = R^2 = R^3 = R^4 = Ph$) in 60% yield by reduction with phosphorus pentasulphide–xylene.[56]

The facile formation of the dibenzoylthiophene (**93**) by 1,3-dipolar cycloaddition of dibenzoylacetylene to the meso-ionic 1,3-thiazol-4-one (**96**) in benzene solution makes tetraphenylthieno[3,4-*c*]thiophene (**89**; $R^1 = R^2 = R^3 = R^4 = Ph$) fairly readily available.[51,60] This preparation of compound **93** undoubtably proceeds via the cycloadduct (**97**), which is not isolated.



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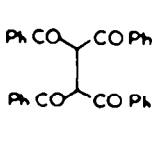

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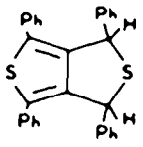

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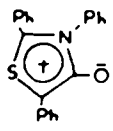

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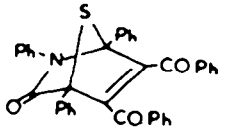
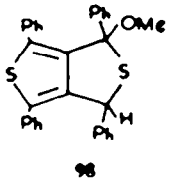


97

Tetraphenylthieno[3,4-*c*]thiophene (**89**; $R^1 = R^2 = R^3 = R^4 = Ph$) is a stable solid. Its nonpolar character is illustrated by the fact that it can be recrystallised from hexane solution. A singlet ground state is indicated by the absence of any ESR absorption in benzene solution[56] and an X-ray crystallographic study has confirmed the symmetrical, planar constitution of the thieno[3,4-*c*]thiophene system[61] (Section VIII, A, a). Catalytic reduction (5% Pd–C) gives the *cis* sulphide (**95**);[56] chromium trioxide oxidation in acetic acid solution gives 3,4-dibenzoyl-2,5-diphenylthiophene (**93**).[56] Treatment with methanol, in the presence of a catalytic amount of sulphuric acid, gives the 2-methoxy sulphide (**98**) which was not isolated but converted to the 2-methoxy sulphone (**99**) in 96% yield by peracetic acid oxidation.[56]

In the absence of oxygen, the tetraphenyl derivative (**89**; $R^1 = R^2 = R^3 = R^4 = Ph$) is photochemically stable. Photo-oxidation in benzene solution (7 hr) gives the dibenzoylthiophene **93** (50%). This product **93** may well arise by the initial formation of the 1,3-adduct (**100**).[56] When much shorter reaction times were used the green monothioketone (**101**) and a yellow product assumed to be the monosulphine (**102**) were also isolated.[56]



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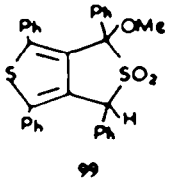

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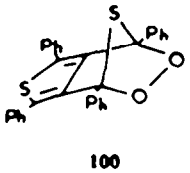

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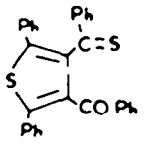

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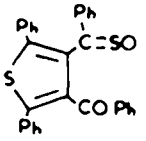
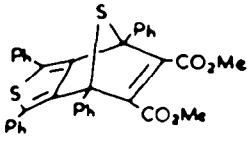


102

The 1,3-dipolar character of tetraphenylthieno[3,4-*c*]thiophene (**89**, $R^1 = R^2 = R^3 = R^4 = Ph$) has already been illustrated by its reaction with N-phenylmaleimide. A similar addition takes place with dimethyl acetylenedicarboxylate in boiling xylene.[56] In this case the cycloadduct (**103**) is not isolated but spontaneous aromatisation occurs giving the isothianaphthene (**104**). A similar reaction using dibenzoylacetylene as 1,3-dipolarophile provides some outstandingly colourful chemistry.[51,60] The *glistening, purple needles* of the tetraphenyl derivative (**89**; $R^1 = R^2 = R^3 = R^4 = Ph$) give the isothianaphthene **105** (61%) as *yellow needles* which upon treatment with phosphorus pentasulphide in boiling pyridine gives *finely matted, blue needles* of hexaphenylthieno[3,4-*f*]isothianaphthene **106** (74%).



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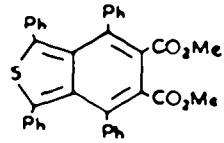

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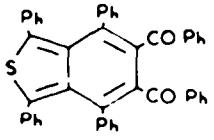

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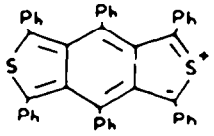
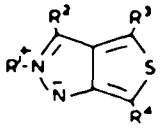
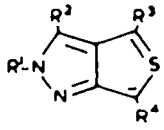


106

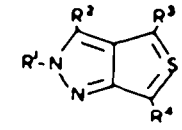
(D) *Thieno*[3,4-*c*]*pyrazoles* (**107**)



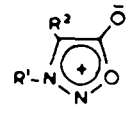
107a



107b



107c



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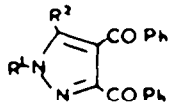


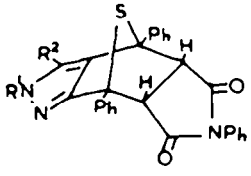
109

An economical preparative route to the thieno[3,4-*c*]pyrazoles (**107**) involves 1,3-dipolar cycloadditon of dibenzoylacetylene to a sydnone (**108**) and treatment of the resulting dibenzoylpyrazole (**109**) with phosphorus pentasulphide in boiling pyridine.[62,63] This sequence

(**108** → **109** → **107**) gives the red-orange, crystalline thieno[3,4-*c*]pyrazoles (**107**) in good yield. Typically, the brick red needles of 2,4,6-triphenylthieno[3,4-*c*]pyrazole (**107**; $R^1 = R^3 = R^4 = Ph$, $R^2 = H$) are quite stable in the solid state but in solution this compound is slowly photo-oxidised to the dibenzoylpyrazole (**109**; $R^1 = Ph$, $R^2 = H$).[63]

In principle the mesomeric betaines (**107**) can participate in 1,3-dipolar cycloaddition reactions either as an azomethine imine (**107a**) or as a thiocarbonyl ylide (**107b**): in practice addition of olefinic and acetylenic dipolarophiles takes place exclusively across the thiocarbonyl ylide fragment (**107b**). With N-phenylmaleimide in toluene at reflux temperature, the triphenyl derivative (**107**; $R^1 = R^3 = R^4 = Ph$, $R^2 = H$) gives a mixture of the *endo*-cycloadduct (**110**; $R^1 = Ph$, $R^2 = H$) (64%) and the *exo*-cycloadduct (**111**; $R^1 = Ph$; $R^2 = H$) (7%). Under the same conditions, the Me derivatives **107** ($R^1 = Me$, $R^2 = H$, $R^3 = R^4 = Ph$) and **107**; ($R^1 = R^3 = R^4 = Ph$, $R^2 = Me$) give exclusively the *endo*-adducts (**110**; $R^1 = Me$ or Ph, $R^2 = H$ or Me). When fumaronitrile was used as dipolarophile, the primary cycloadduct (benzene, 44%; xylene, 7%) was thermally unstable giving 5,6 - dicyano - 2,4,7 - triphenyl - 2H-indazole (**112**) by elimination of hydrogen sulphide.[63]

With dimethylacetylenedicarboxylate, thieno[3,4-*c*]pyrazoles (**107**) give 5,6 - bis - (methoxycarbonyl) - 2 - H - indazoles (**113**; $R^3 = MeO$) without isolation of the thermally unstable, intermediate adduct (**114**) which readily aromatises by loss of elemental sulphur. Use of dibenzoylacetylene provides a route to the novel thieno[3,4-*f*]-2H-indazole system (**115**). Thus, compound **107** ($R^1 = R^3 = R^4 = Ph$, $R^2 = H$) with dibenzoylacetylene gives the 5,6 - dibenzoyl - 2H - indazole (**113**; $R^1 = Ph$, $R^2 = H$, $R^3 = Ph$) which with P_4S_{10}-pyridine gives compound **115**.[63] The novel compound **115** is an example of a tricyclic mesomeric betaine. With N-phenylmaleimide it gives the 1,3-dipolarcycloadduct (**116**).[63]



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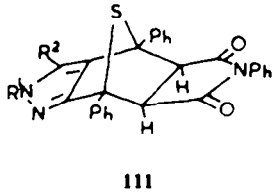

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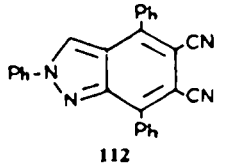

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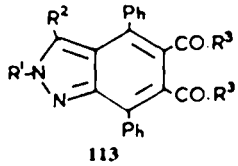

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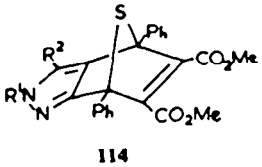

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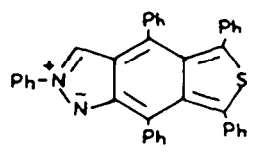

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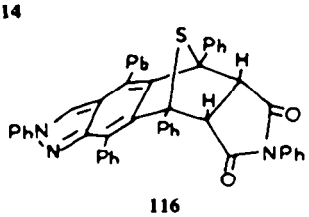
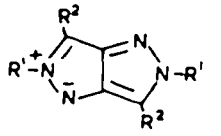
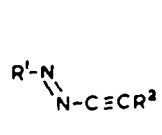


116

(E) *Pyrazolo*[4,3-*c*]*pyrazoles* (**117**)



117



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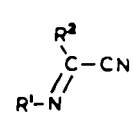


119

The isolation of very stable pyrazolo[4,3-*c*]pyrazole derivatives (**117**) demonstrates that the participation of *d*-orbitals in the bonding of type A mesomeric betaines of general structure **37** is not essential.

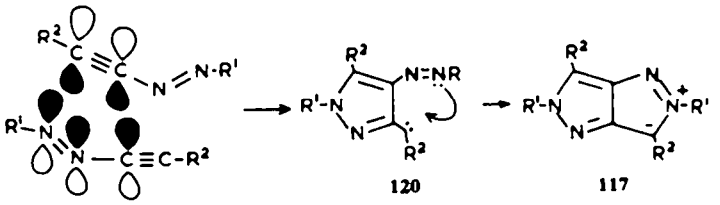
The preparation of these compounds (**117**) involves a fascinating dimerisation of arylazoethynylarenes (**118**), which is achieved in boiling cyclohexane solution.[64,65] Typically, *p*-chlorophenylazoethynylbenzene (**118**; $R^1 = p\text{-}Cl\text{-}C_6H_4$, $R^2 = Ph$) gives pale yellow crystals of the pyrazolo[4,3-*c*]pyrazole (**117**; $R^1 = p\text{-}Cl\text{-}C_6H_4$, $R^2 = Ph$), m.p. 328°, in 60% yield. Another study[66] has demonstrated that *bis*-arylazoacetylenes (ArN=N·C≡C·N=NAr), generated *in situ* by base catalysed dehydrohalogenation of the *bis*-hydrazidehalides (ArNH·N=CCl·CCl=N·NHAr), also dimerise to pyrazolo[4,3-*c*]pyrazole derivatives (**117**; $R^1 = Ph$ or $o\text{-}Me\text{-}C_6H_4$, $R^2 = N{=}N\text{·}R^1$).

The mechanism of this novel dimerisation (**118** → **117**) is worthy of some consideration. The reaction can be regarded as the cycloaddition of an acetylene to the C-N=N fragment of the arylazoethynylarene (**118**) giving the carbene species (**120**) which rapidly gives the bicyclic product **117** (Scheme 1). A more pleasing alternative is the possibility that the product is formed in a single concerted process in which the acetylenic function of each molecule simultaneously adds to the C-N=N fragment of its partner (Scheme 2). This type of cycloaddition is not without precedent. For example, the *bis*-arylazoacetylenes react with olefines giving the cycloadducts **121** (Scheme 3).[66] The process **118** → **117** (Schemes 1 and 2) is also closely related to the *criss-cross* cycloaddition[67] of olefines to azines (Scheme 4).[68,69]

The mechanism of formation of compound **117** ($R^1 = p\text{-}Cl\text{-}C_6H_4$, $R^2 = Ph$) is undoubtably closely related to the mechanism of its thermal fragmentation.[64,65] Thus, vacuum pyrolysis of this derivative (**117**; $R^1 = p\text{-}Cl\text{-}C_6H_4$, $R^2 = Ph$) at 500° gives a 30% yield of α-(*p*-chlorophenylimino)phenylacetonitrile (**119**; $R^1 = p\text{-}Cl\text{-}C_6H_4$, $R^2 = Ph$).[64,65] This cycloreversion (**117** → **119**) is clearly analogous to the dimerisation (**118** → **117**).

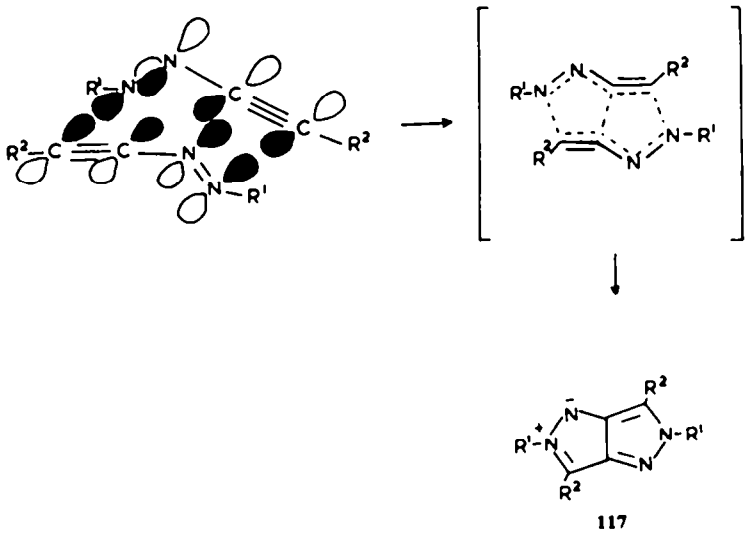
An alternative synthetic route to the mesomeric betaines (**117**) involves heating a 3 - benzoyl - 4 - arylazopyrazole (**122**) with triethyl phosphite.[70,71] The mechanism of this reaction (Scheme 5) may proceed via the carbene species (**124**)[70]—a possible intermediate in the previous synthesis (**120**; Scheme 1). However, it is equally probable that the intermediate oxyphosphonium zwitterion (**123**) cyclises directly to the product **117** without involvement of the free carbene **124** (Scheme 5).[71]

The pyrazolo[4,3-*c*]pyrazoles (**117**) are extremely stable, crystalline compounds with high m.ps. They are sparingly soluble in organic solvents giving fluorescent solutions.[65] The 2,5-di-*p*-chlorophenyl derivative (**117**; $R^1 = p\text{-}Cl\text{-}C_6H_4$, $R^2 = Ph$) dissolves in concentrated sulphuric acid but is reprecipitated upon dilution.[65] With nitric acid in concentrated sulphuric acid solution, nitration of the phenyl substituents occurs giving the dinitro



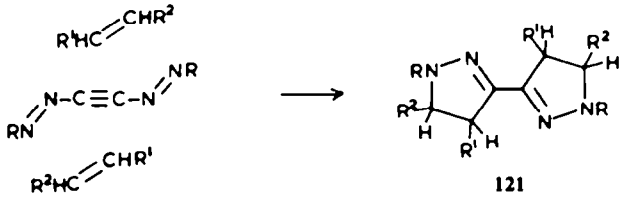
120 117

Scheme 1.



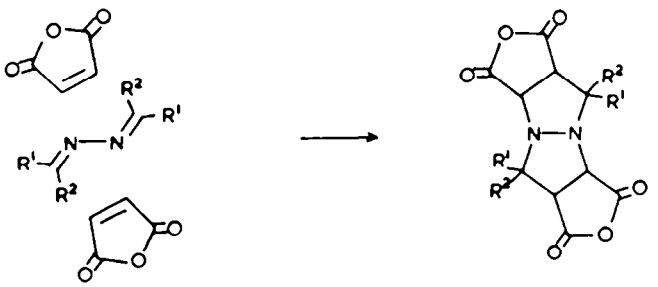
117

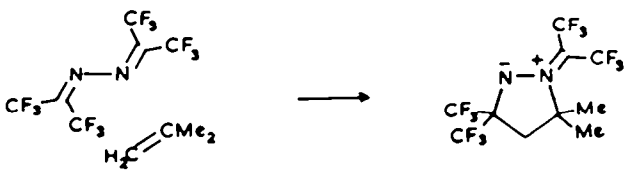
Scheme 2.



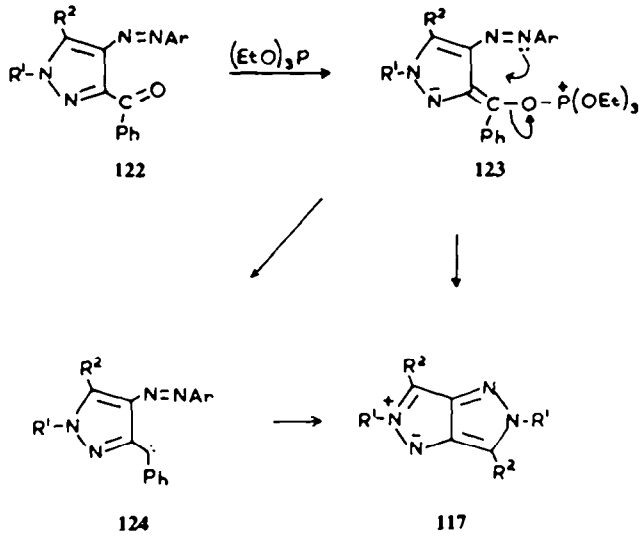
121

Scheme 3.





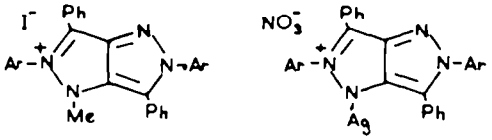
Scheme 4.



122 123 124 117

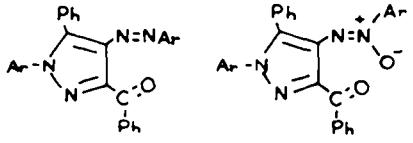
Scheme 5.

derivative (**117**; $R^1 = p\text{-}Cl\text{-}C_6H_4$, $R^2 = p\text{-}NO_2\text{-}C_6H_4$). Similarly, bromination in chloroform solution gives the monobromo derivative (**117**; $R^1 = p\text{-}Cl\text{-}C_6H_4$, $R^2 = p\text{-}Br\text{-}C_6H_4$ or Ph; 38%) and the dibromo derivative (**117**; $R^1 = p\text{-}Cl\text{-}C_6H_4$, $R^2 = p\text{-}Br\text{-}C_6H_4$; 6%).[65] Heating with methyl iodide for one week gives an orange, crystalline methiodide (**125**; $Ar = p\text{-}Cl\text{-}C_6H_4$); treatment with silver nitrate gives a 1 : 1 adduct (**126**; $Ar = p\text{-}Cl\text{-}C_6H_4$).[65]

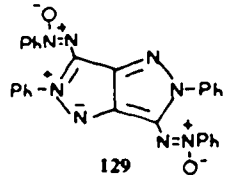


125 126

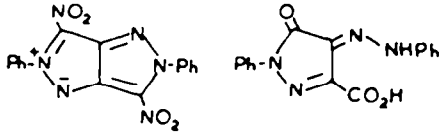
Oxidation of the pyrazolo[4,3-*c*]pyrazole (**117**; $R^1 = p\text{-}Cl\text{-}C_6H_4$, $R^2 = Ph$) with either potassium permanganate in aqueous pyridine[65,70] or peroxyacetic acid in chloroform[65] gives the 3 - benzoyl - 4 - arylazopyrazole (**127**; $Ar = p\text{-}Cl\text{-}C_6H_4$). When peroxybenzoic acid was used as oxidising agent, further oxidation to the azoxy derivative (**128**; $Ar = p\text{-}Cl\text{-}C_6H_4$) occurred.[70] The phenylazo derivative (**117**; $R^1 = Ph$, $R^2 = N{=}NPh$) is converted to the azoxy derivative (**129**) by hydrogen peroxide, whereas treatment of the same compound with nitric acid gives the dinitro derivative (**130**).[66] The latter product (**130**) is oxidised to the pyrazolone (**131**) by hydrogen peroxide.[66]



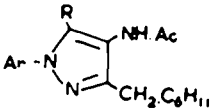
127 128



129

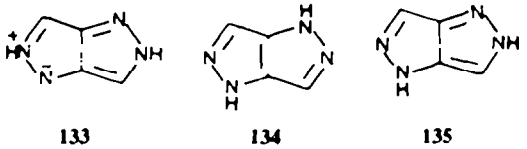


130 131

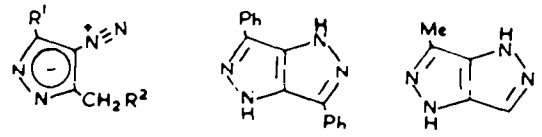


132

Catalytic hydrogenation (platinum oxide) of compound **117** ($R^1 = p\text{-}Cl\text{-}C_6H_4$, $R^2 = Ph$) in acetic acid solution gave a mixture of the pyrazoles **132** ($Ar = p\text{-}Cl\text{-}C_6H_4$, $R = Ph$; 25%) and **132** ($Ar = p\text{-}Cl\text{-}C_6H_4$, $R = C_6H_{11}$; 10%).[64,65]



133 134 135



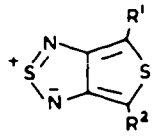
136 137 138

As far as we are aware, the parent molecule, 2H,5H-pyrazolo[4,3-*c*]pyrazole (**133**) has not been encountered and the relative energy of the tautomeric structures (**133–135**) is unknown. Almost certainly the mesomeric betaine (**133**) is the least stable of the tautomeric forms (**133–135**). The preparation of tautomeric species has been reported. Thermal isomerisation of the diazopyrazole (**136**; $R^1 = R^2 = Ph$) in acetic acid solution gives a colourless, high melting product (> 300°) formulated as the classical tautomer (**137**).[72] A similar transformation

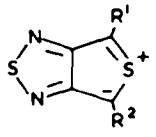
of 4 - diazo - 3,5 - dimethylpyrazole (**136**; R^1 = Me, R^2 = H) gives compound **138**[73] (wrongly formulated in a recent review).[74]

1,3-Dipolarcycloaddition reactions of pyrazolo[4,3-*c*]pyrazoles (**117**) have *not* been reported.

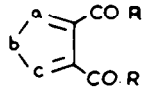
(F) *Thieno*[3,4-*c*]-1,2,5-*thiadiazoles* (**139**)



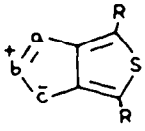
139a



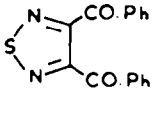
139b



140



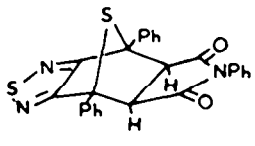
141



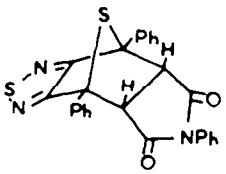
142

The cyclothiation of 1,2-diaroyl heterocycles (**140**) to the corresponding bicyclic thiophene derivative (**141**) using phosphorus pentasulphide is now an established route to these mesomeric betaines (**141**). The preparation of 2,5-diphenylthieno[3,4-*c*]-1,2,5-thiadiazole (**139**; R^1 = R^2 = Ph), m.p. 146°, in 78% yield by treatment of 3,4 - dibenzoyl - 1,2,5 - thiadiazole (**142**) with phosphorus pentasulphide in dioxan at reflux temperature[75] appears to have been the first reported example of this general synthetic route (**140** → **141**).

Compound **139** (R^1 = R^2 = Ph) is obtained as brilliant purple needles (λ_{max} 558 nm (ϵ 8650)) whose structure is fully supported by its mass spectrum [*m/e* 294, $M^{+\cdot}$ and 121, PhC≡S$^+$].[75] A *sluggish* cycloaddition takes place with N-phenylmaleimide at 140° giving a mixture of the *exo* and *endo* cycloadducts (**143** and **144**). The major product (48%), m.p. 217°, has been assigned the *exo* structure (**143**) and the minor product (24%), m.p. 213°, has been assigned the *endo* structure (**144**).[75] These structural assignments (**143** and **144**)[75] are based on the understanding that the bridgehead phenyls of the *exo* adduct (**143**) substantially deshield the protons located α to the CO groups. More recent NMR studies[76,77] of *endo*/*exo* cycloadducts of 1,3-diphenylisobenzofuran suggest that this type of deshielding by bridgehead phenyl substituents does not occur. It is conceivable, therefore, that the structural assignments (**143** and **144**)[75] should be reversed. A similar reassignment of the structures of cycloadducts of thieno[3,4-*c*]thiophenes (**89**)[56] and thieno[3,4-*c*]pyrazoles (**107**)[63] has already been made.

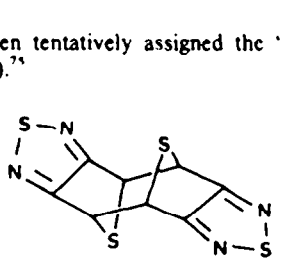


143



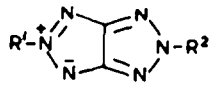
144

Photolysis of a methylene chloride solution of 2,5-diphenylthieno[3,4-*c*]-1,2,5-thiadiazole (**139**; R^1 = R^2 = Ph) gives a colourless dimer, m.p. 100° (*m/e* 588, $M^{+\cdot}$) which has been tentatively assigned the '*head to tail*' structure (**145**).[75]



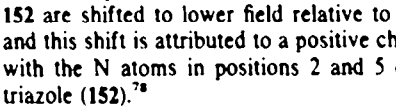
145

(G) 1,2,3-*Triazolo*[4,5-d]-1,2,3-*triazoles* (**146**)

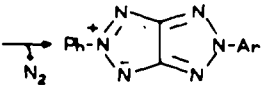


146

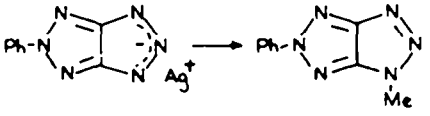
Representatives of the triazolotriazoles (**146**) have been prepared by two methods.[78] Diazotisation of the amines (**147**) and subsequent treatment with sodium azide gives 4 - azido - 5 - arylazo - 2 - phenyl - 1,2,3 - triazoles (**148**) which upon gentle heating give an almost quantitative yield of the mesomeric betaines (**149**) together with elimination of nitrogen.[78] In a second method, methylation of the silver salt (**150**) using methyl iodide gives a mixture of the N-Me isomers **151** (m.p. 139°) and **152** (m.p. 149°) which can be separated by thin layer chromatography. The mesomeric betaine structure (**152**) is assigned to the higher melting isomer on the basis of its NMR spectrum. All the proton signals of compound **152** are shifted to lower field relative to the isomer **151** and this shift is attributed to a positive charge associated with the N atoms in positions 2 and 5 of the triazolotriazole (**152**).[78]



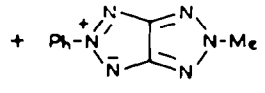
147 **148**



149



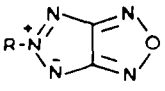
150 **151**



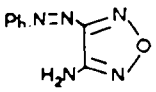
152

The "*hexa-azapentalenes*" (**146**) are resistant to oxidation.[79] Catalytic hydrogenation of the diphenyl derivative (**146**; R^1 = R^2 = Ph) did not reduce the azapentalene nucleus; the products were the mono and dicyclohexyl derivatives **146** (R^1 = Ph, R^2 = C_6H_{11}) and **146** (R^1 = R^2 = C_6H_{11}).[78]

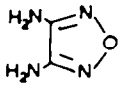
(H) 1,2,3-*Triazolo*[4,5-c]-1,2,5-*oxadiazoles* (**153**)



153



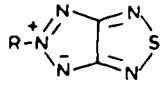
154



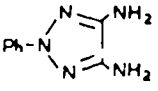
155

Lead tetraacetate oxidation of 3 - amino - 4 - phenylazo - 1,2,5 - oxadiazole (**154**), prepared from 3,4 - diamino - 1,2,5 - oxadiazole (**155**) and nitrosobenzene, gives the yellow, crystalline phenyl derivative (**153**; R = Ph).[79] This reaction presumably occurs via an intermediate nitrene. Compound **153** (R = Ph), the only known representative of this heterocyclic system (**153**), is resistant to oxidation by *m*-chloroperoxybenzoic acid.[79]

(I) 1,2,3 - *Triazolo* - [4,5-c] - 1,2,5 - *thiadiazoles* (**156**)



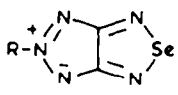
156



157

2 - Phenyl - 1,2,3 - triazolo - [4,5-c] - 1,2,5 - thiadiazole (**156**: R = Ph) has been prepared by treatment of 4,5 - diamino - 2 - phenyl - 1,2,3 - triazole (**157**) with sulphur monochloride.[79] The reverse process (**156** → **157**) is achieved at room temperature by reduction with lithium aluminium hydride. Compound **156** (R = Ph) is not oxidised by *m*-chloroperoxybenzoic acid or hydrogen peroxide but extensive oxidation, giving no well defined products, is observed using potassium permanganate. This yellow, crystalline derivative **156** (R = Ph) is fully characterised by its spectral properties.[79]

(J) 1,2,3 - *Triazolo*[4,5-c] - 1,2,5 - *selenadiazoles* (**158**)

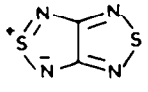


158

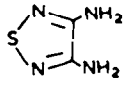
4,5 - Diamino - 2 - phenyl - 1,2,3 - triazole (**157**) has been converted to the mesomeric betaine (**158**; R = Ph) by treatment with selenous acid (H_2SeO_3).[79] This yellow triazoloselenadiazole (**158**; R = Ph), m.p. 204°, shows a mass spectrum [*m/e* 251 ($M^{+\cdot}$), 105 (PhN_2^+)] consistent with the bicyclic structure (**158**), and this structure is further supported by its UV and NMR spectra and its half-wave reduction potential. These physical properties are similar to those of the isoelectronic chalcogen derivatives **153** and **156**.[79]

No reactions of this selenium heterocycle (**158**; R = Ph) have been reported.

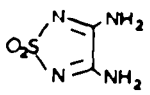
(K) 1,2,5 - *Thiadiazolo*[3,4-c] - 1,2,5 - *thiadiazole* (**159**)



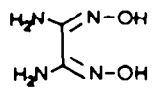
159



160



161



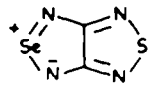
162

The thiadiazolothiadiazole (**159**) has been prepared by several similar methods.[80] Treatment of either 3,4 - diamino - 1,2,5 - thiadiazole (**160**) or the corresponding sulphone (**161**) with sulphur monochloride in dimethylformamide solution gives, in good yield, colourless prisms, m.p. 116°, of this novel heterobicycle (**159**). Other chlorides of sulphur ($SOCl_2$–pyridine; SCl_2–DMF) have also been used to achieve this cyclisation. Alternatively, and more conveniently, compound **159** can be prepared in 66% yield by cyclisation of the dioxime of oxamide (**162**) using sulphur dichloride in DMF at 55°.

The bicyclic structure (**159**) has been confirmed by an X-ray structural analysis (Section VIII, A, b);[81] the ^{13}C NMR spectrum shows a single line at 169.4 ppm from tetramethylsilane.[80] Further structural evidence is provided by the mass spectral fragmentation pattern [*m/e* 143.9563 ($M^{+\cdot}$; 100%) → *m/e* 72 ($N{\equiv}C{-}N^{+\cdot}{=}S$; 37%), *m** 36 and *m/e* 46 ($N{\equiv}S^+$; 63%), *m** 14.7] although a fragment ion at *m/e* 77.94708 (NS_2^+; 34%) is more difficult to account for.[80]

Hydrolysis of compound **159** gives 3,4 - diamino - 1,2,5 - thiadiazole (**160**) and sulphur dioxide.[80] However, in the presence of sulphurous acid, the thiadiazole (**160**) is further hydrolysed giving oxamide ($H_2N{\cdot}CO{\cdot}CO{\cdot}NH_2$) and elemental sulphur. Consequently, in the hydrolysis of compound **159** a mixture of the thiadiazole (**160**), oxamide and sulphur is usually obtained. Hydrolysis in dilute ammonium hydroxide prohibits the second step (**160** → oxamide) and under these conditions the 3,4 - diamino - 1,2,5 - thiadiazole (**160**) is formed in almost quantitative yield.[80]

(L) 1,2,5 - *Selenadiazolo*[3,4-c] - 1,2,5 - *thiadiazole* (**163**)



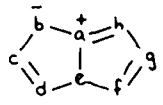
163

Treatment of 3,4 - diamino - 1,2,5 - thiadiazole (**160**) with selenium oxychloride ($SeOCl_2$) has been reported to give the selenadiazolo[3,4-c]thiadiazole (**163**) as a pale orange solid. The structural assignment (**163**) is supported by IR and low resolution mass spectra.[82]

V. HETEROPENTALENE MESOMERIC BETAINES OF TYPE B

In the general structure **38**, the atoms a and e must necessarily be N atoms. If the remaining atoms, b, c, d, f, g, h are either N or a substituted C atom (CR) then it can be shown that 24 distinct structural types are possible. Representatives of four of these types are known and these are now discussed in the order given in Table 2. The synthesis of new examples of type B heteropentalene mesomeric betaines (**38**) can be expected although not all the 24 possibilities can be expected to be stable. It is unlikely that a new allotrope of nitrogen having the structure **38** (a = b = c = d = e = f = g = h = N) will be isolated in the near future.

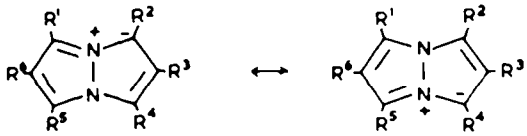
Table 2. Known mesomeric heteropentalenes of type B (38)



Parent system	Heterocycle	Atom or group*							
		a	b	c	d	e	f	g	h
Pyrazolo[1,2-*a*]pyrazoles	(164)	N	CR	CR	CR	N	CR	CR	CR
Pyrazolo[1,2-*a*]-1,2,3-triazoles	(179)	N	CR	CR	CR	N	CR	CR	N
1,2,3-Triazolo[1,2-*b*]-1,2,3-triazoles	(206)	N	CR	CR	N	N	CR	CR	N
1,2,3-Triazolo[1,2-*a*]-1,2,3-triazoles	(226)	N	N	CR	CR	N	CR	CR	N

*The groupings a and e each contribute 2 electrons to the π-electron system of the heterocycle; b, c, d, f, g and h each contribute 1 electron.

(A) *Pyrazolo*[1,2-a]*pyrazoles* (**164**)

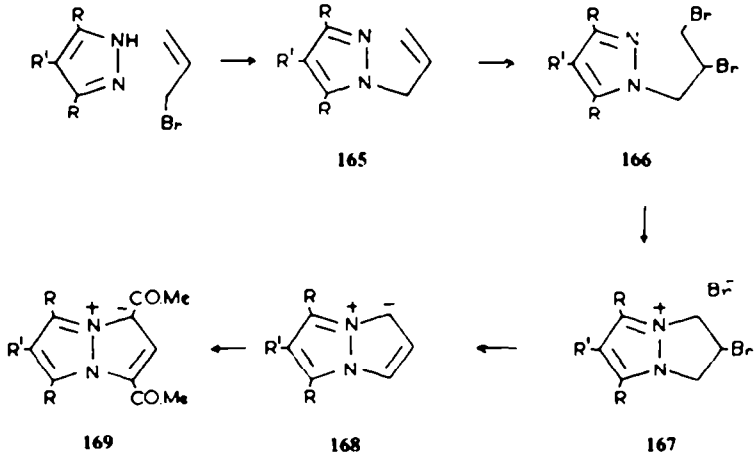


164a **164b**

The pyrazolo[1,2-*a*]pyrazoles (**164**), the most fundamental derivatives of the type B mesomeric betaines, have been prepared from pyrazoles by two routes. Particularly useful is a synthesis employing 1-allylpyrazoles **165** (Scheme 6)[83-86] since this route has been used to prepare the parent compound (**164**; $R^1 = R^2 = R^3 = R^4 = R^5 = R^6 = H$). In general, bromination of 1-allylpyrazoles (**165**) and thermal cyclisation of the crude product (**166**) gives the bicyclic bromides (**167**) which upon treatment with aqueous alkali yield the pyrazolopyrazoles **168** (Scheme 6). This method[83,86] has been used to prepare the parent compound **168** (R = R' = H), the 2-bromo derivative (**168**; R = H, R' = Br) and the 1,2,3-trimethyl derivative (**168**; R = R' = Me) and a similar sequence using 1-cinnamylpyrazole[84,86] has yielded the 1-phenyl derivative (**164**; $R^1 = Ph$, $R^2 = R^3 = R^4 = R^5 = R^6 = H$). Electron-withdrawing groups on the pyrazole ring (e.g. **166**; R = H, R' = CN or R = R' = Br) inhibit the intramolecular cyclisation (**166** → **167**).[84]

The pyrazolopyrazoles (**168**) prepared by this method[83-86] are colourless solids which appear to be stable in aqueous solution. However, they are extremely sensitive to air, rapidly giving intensely coloured oxidation products. Their bicyclic structure (**168**) is fully supported by their spectroscopic properties. For example the A_2X NMR spectrum of the unsubstituted derivative (**168**; R = R' = H) [τ 2.95(d) and 3.52(t), *J* 2.5 Hz][85] is consistent with a structure in which resonance places negative charge in the 1 and 3 positions. Indeed, electrophilic substitution readily takes place at these positions giving 1,3-disubstituted derivatives.[83,84] Treatment with acetic anhydride gives 1,3-diacetyl compounds **168** → **169** (Scheme 6) and similar electrophilic substitutions occur with benzoyl chloride and cyanogen chloride. These substituted derivatives (e.g. **169**) are considerably more stable than their precursors (**168**) being stable in air for periods of up to 2 years.[83,84]

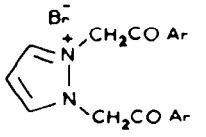
The first reported synthesis of a pyrazolo[1,2-*a*]pyrazole derivative[87,88] involved alkylation of pyrazole with phenacyl bromide giving the dialkylated salt (**170**). Cyclodehydration of this bromide (**170**) using 10% aqueous sodium bicarbonate at 50° gave a 98% yield of the yellow, crystalline mesomeric betaine (**171**): a reaction reminiscent of the Tschitschibabin indolizine synthesis.[89] When *p*-bromophenyl and *m*-nitrophenyl derivatives (**171**; Ar = *p*-Br·C_6H_4 and *m*-NO_2·C_6H_4) were prepared by this method, the strongly H-bonded intermediate hydrates (**172**) could be intercepted.[88] The *p*-chlorophenyl



165 **166** **167** **168** **169**

Scheme 6.

derivative (171; Ar = *p*-Cl·C$_6$H$_4$) is debenzoylated by hot concentrated hydrochloric acid giving the chloride (173) which upon treatment with lithium hydride gave the air sensitive pyrazolo[1,2-*a*]pyrazole (164; R^1 = *p*-Cl·C$_6$H$_4$, R^1 = R^2 = R^4 = R^5 = R^6 = H).[86]



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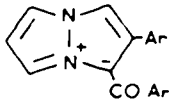

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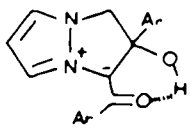

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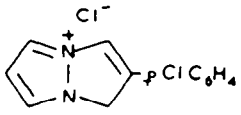
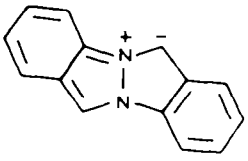


173

Dibenzo derivatives of the pyrazolo[1,2-*a*]pyrazoles (174) have not been reported. The valence tautomers, dibenzo[*b,f*] [1,5] diazocines (175), are known[90-95] and it has been claimed that they have contraceptive properties.[96-99] The structure of the unsubstituted derivative (175) has been firmly established and cyclisation to the valence tautomer (175 → 174) is clearly unfavourable.[100]



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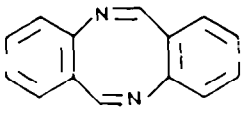
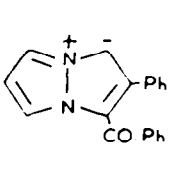


175

The pyrazolo[1,2-*a*]pyrazoles (164) can be regarded as possessing an azomethine ylide 1,3-dipole within its ring system, and these molecules (164) do in fact participate in 1,3-dipolar cycloaddition reactions. The 1 - benzoyl - 2 - phenyl derivative (176) and dimethyl acetylenedicarboxylate give the adduct (177) which is not isolated but dehydrogenated *in situ* (Pd/carbon) giving the novel 8-azacycl-[2,2,2]-azine (178).[47]



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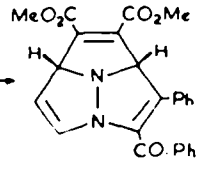

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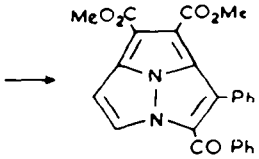
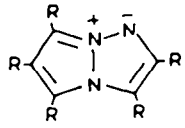


178

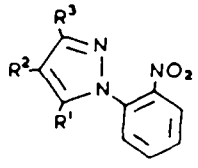
With tetracyanoethylene, the pyrazolopyrazoles (164) give a brilliant red colouration which provides a convenient qualitative test but the structure of this product has not been examined.[84] The parent compound (164; R^1 = R^2 = R^3 = R^4 = R^5 = R^6 = H) has been reported to react with dimethyl acetylenedicarboxylate, dimethyl azodicarboxylate and acrylonitrile but the nature of the products was not investigated.[84]

(B) *Pyrazolo*[1,2-a]-1,2,3-*triazoles* (179)



179

Although examples of the bicyclic pyrazolo[1,2-*a*]triazoles (179) are not known, monobenzo derivatives (181) and dibenzo derivatives (183) have been prepared by reductive cyclisation of 1-(*o*-nitroaryl)pyrazoles (180 → 181)[101-103] and 1-(*o*-nitroaryl) indazoles (182 → 183)[48,104] using triethyl phosphite. Pyrazolo[1,2-*a*]benzotriazole (181; R^1 = R^2 = R^3 = H)[101] is obtained as cream prisms, m.p. 102–103°, and the dibenzo derivative (183; R^1 = R^2 = R^3 = R^4 = H)[104] as yellow prisms, m.p. 158–159°. In a similar manner, derivatives of the general types 184[48] and 185[105] have also been synthesised.



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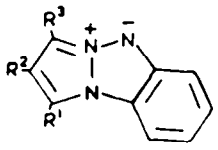

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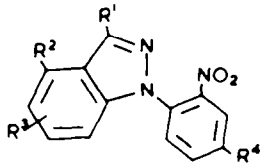

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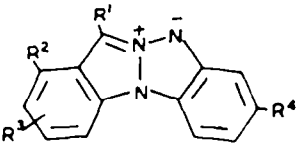

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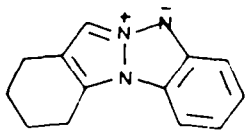

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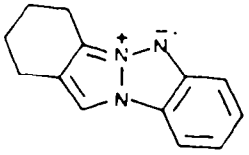
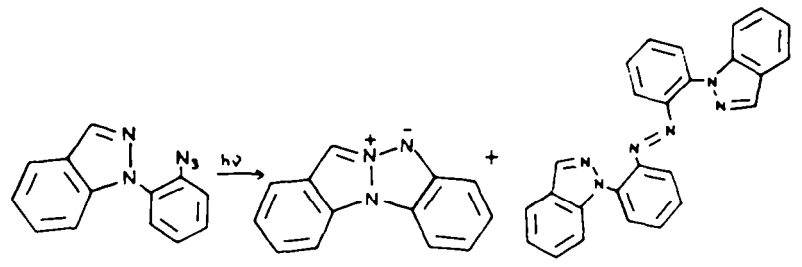
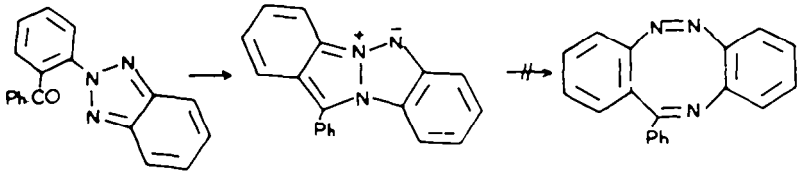


185

An alternative route to the dibenzo compound (187) involves the photolysis of 1-(*o*-azidophenyl)-indazole (186); a reaction which gives 187 (23%) together with 2,2' - di(1 - indazolyl)azobenzene 188 (20%).[104] A representative of the isomeric dibenzo system (190) has been prepared by reductive cyclisation of 2 - (*o* - benzoylphenyl) - benzotriazole (189) with triethyl phosphite.[71] This compound (190) does not apparently ring open to the valence tautomer (191).



186 187 188

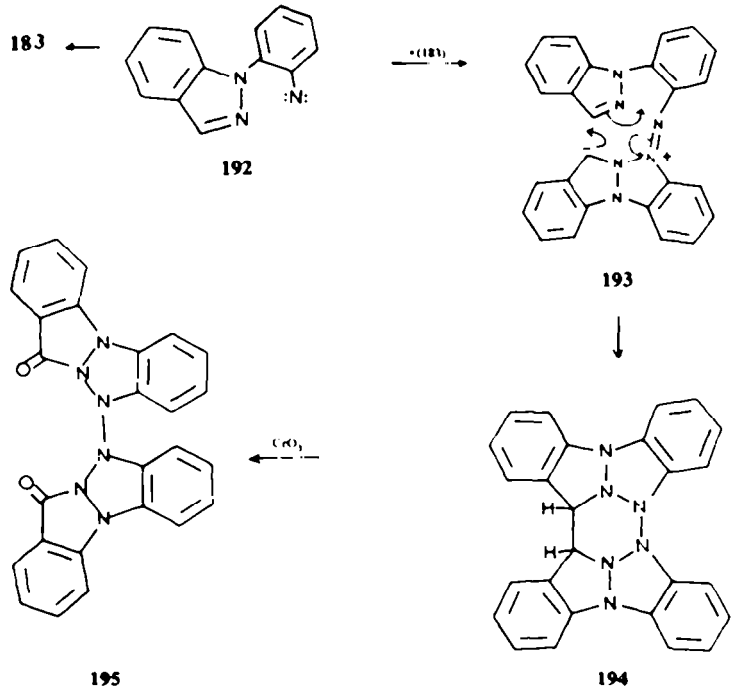


189 190 191

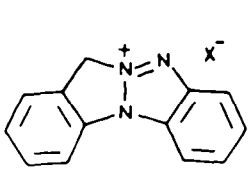
The most extensively studied pyrazolo[1,2-*a*]triazoles are the dibenzo derivatives, prepared by the sequence **182**→**183**.[48] This preparation gives moderate yields (10–30%) of the mesomeric betaines (**183**). A second product is often encountered and this has been assigned the remarkable dimeric structure **194** (Scheme 7). Indeed, this structure (**194**) is supported by its spectral properties and by the observation that chromic acid oxidation gives 6,6′ - bis(12 - oxoindazolo - [1,2-*a*] - benzotriazolyl) (**195**).[48,104] The mechanism of formation of this *dimeric* product can be rationalised in formal terms by the participation of an intermediate nitrene (**192**) which can either collapse to the pyrazolo[1,2-*a*]triazole (**183**) or alternatively may react with a previously formed molecule of **183**. The resulting dipolar intermediate (**193**) may then undergo an intramolecular 1,4-dipolar cycloaddition[106] (**193**→**194**) giving the observed product **194** (Scheme 7). The possibility that the pyrazolotriazoles (**183**) dimerise under the conditions of the reaction has been eliminated (**183**→**194**).[104]

The dibenzo derivatives (**183**; R^1 = H) form salts (**196**) with strong acids ($HClO_4$, HBF_4, $CF_3{\cdot}CO_2H$) and undergo electrophilic substitution at position 7.[107] Under Vilsmeier–Haack conditions ($Me_2N{\cdot}CO{\cdot}R{\cdot}POCl_3$ at 0°) the 7-formyl (**197**; R^1 = H) and 7-acetyl (**197**; R^1 = Me) derivatives are formed. Similarly, trifluoroacetic anhydride or *p*-nitrobenzoyl chloride in carbon tetrachloride at room temperature give 7-trifluoroacetyl (**197**; $R^1 = CF_3$) and 7-*p*-nitrobenzoyl (**197**; $R^1 = p{\cdot}NO_2{\cdot}C_6H_4$) derivatives.[107]

The dibenzo pyrazolo[1,2-*a*]triazoles (**183**) participate in 1,3-dipolar cycloaddition reactions and this is an aspect of their chemistry which is particularly interesting, not only because of the nature of the azomethine



Scheme 7.



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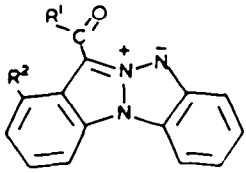
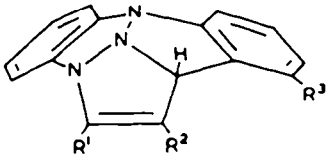


197

imine 1,3-dipole but also because of the novel structure of the adducts (**198**) and their potential use as synthetic intermediates.



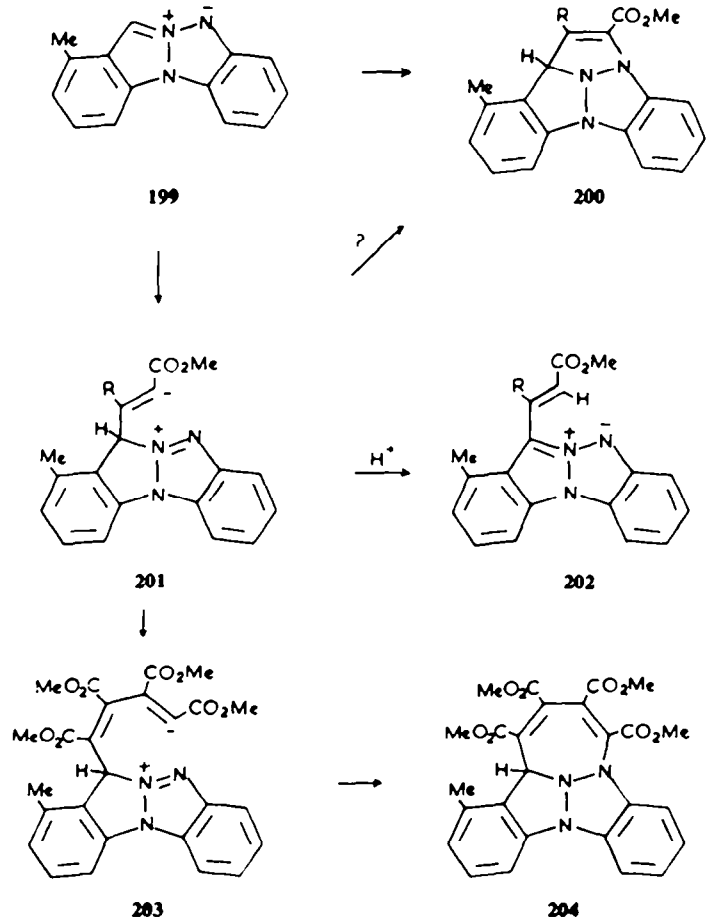
198

The reactions of the 8-Me derivative (**199**) with acetylenic dipolarophiles have been studied in some detail.[108,109] With dimethyl acetylenedicarboxylate, diethyl acetylenedicarboxylate and diphenylacetylene, the yellow crystalline adducts (**198**; $R^1 = R^2 = CO_2Me$, CO_2Et, Ph, $R^3 = Me$) are formed.[108] Similarly, regiospecific additions take place with methyl and ethyl propiolate, phenylacetylene and *p*-chlorophenylacetylene; and methyl phenylpropiolate gives a mixture of two regio-isomers.[109]

In the cycloaddition of compound **199** with one equivalent of dimethyl acetylenedicarboxylate, the cycloadduct (**200**; $R = CO_2Me$) is accompanied by a second product which has been found to have the structure **202** ($R = CO_2Me$).[108] The mechanism of formation of this Michael adduct (**202**; $R = CO_2Me$) presumably involves the initial formation of the dipolar intermediate **201** ($R = CO_2Me$; Scheme 8) which then gives the product **202** ($R = CO_2Me$) by proton transfer. Alternatively the zwitterion (**201**; $R = CO_2Me$) may collapse to give the cycloadduct **200** ($R = CO_2Me$; Scheme 8); the extent to which the cycloadducts (**200**) are formed by this type of mechanism (**201** → **200**) rather than by a truly concerted 1,3-dipolar cycloaddition (**199** → **200**) is open to conjecture.

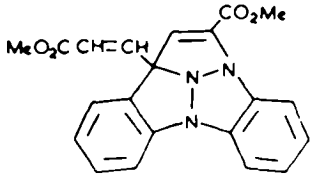
When compound **199** is reacted with two equivalents of dimethyl acetylenedicarboxylate, a different product is formed in high yield and this has been tentatively assigned the structure **204**.[108] The formation of this product is reasonably rationalised by the sequence **201** → **203** → **204** (Scheme 8); a mechanism which has ample precedent in the reactions of dimethyl acetylenedicarboxylate with pyridine,[106,110] isoquinoline[106,111] and other heterocycles.[112,113]

Using one equivalent of methyl propiolate ($HC{\equiv}C{\cdot}CO_2Me$), compound **199** again forms two ad-



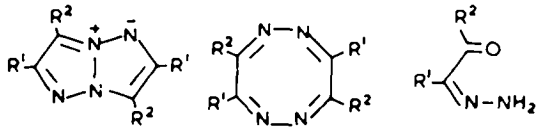
Scheme 8.

ducts, **200** (R = H) and **202** (R = H).[109] The tricyclic adduct **200** (R = H) has been subject to a detailed NMR study including deuterium labelling; the second adduct (**202**; R = H) has been prepared by an alternative route involving the reaction of the 7-formyl derivative (**197**; R^1 = H, R^2 = Me) with diethyl methoxycarbonylmethylphosphonate [$(EtO)_2PCH_2CO_2Me$].[109] With two equivalents of methyl propiolate a quantitative yield of the 1:2 adduct (**205**) is obtained. This product (**205**) is also obtained by treatment of the primary adduct (**200**; R = H) with methyl propiolate but cannot be obtained from the Michael adduct (**202**; R = H).[109]



205

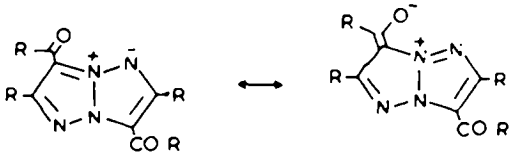
(C) 1,2,3 - *Triazolo*[1,2-b] - 1,2,3 - *triazoles* (**206**)



206 **207** **208**

Representatives of the 1,2,3 - triazolo[1,2-*b*] - 1,2,3 - triazoles (**206**) were first prepared in 1956[114,115] but at first their bicyclic structure was not recognised and they were formulated as the isomeric tetraazacycloöctatetraenes (**207**). The methods of preparation of these compounds (**206**) are based upon the cyclic condensation of hydrazones with carbonyl functions; reactions which might reasonably be expected to give the valence tautomers (**207**). These synthetic routes are conveniently illustrated by two preparations of the tetraphenyl derivative (**206**; $R^1 = R^2$ = Ph). Metze[114] in 1956 showed that benzil monohydrazone (**208**; $R^1 = R^2$ = Ph), when heated above its m.p., gave a compound, m.p. 278°, which was later recognised as the tetraphenyltriazolotriazole (**206**; $R^1 = R^2$ = Ph). The same product was also prepared in 1960 by Schlesinger[116] who heated benzil (PhCO·CO·Ph) with an equimolar quantity of its dihydrazone. In both these methods of preparation it seems reasonable to suppose that the tetraazacycloöctatetraene (**207**) is initially formed but rapidly cyclises to the more stable isomer (**206**).

Using the methods illustrated above, a large number of derivatives of the tetraazapentalenes (**206**) have been prepared.[114-120] Heating the hydrazone of methyl benzoylglyoxylate (**208**; $R^1 = CO_2Me$, R^2 = Ph) gives only compound **206** (R^1 = Ph, $R^2 = CO_2Me$)[115,117] although in principle the isomeric product **206** ($R^1 = CO_2Me$, R^2 = Ph) might also be expected. Similarly the hydrazone **208** ($R^1 = CO_2Et$, R^2 = Me) gives compound **206** (R^1 = Me, $R^2 = CO_2Et$).[118-120] The formation of a single isomer can be attributed to the greater thermodynamic stability of the observed product. The carboalkoxy groups in positions 3 and 6 can stabilise the mesomeric betaine by resonance interaction (**209**↔**210**); an interaction which cannot occur in the isomers **206** (R^1 = RCO, R^2 = Me or Ph).



209 **210**

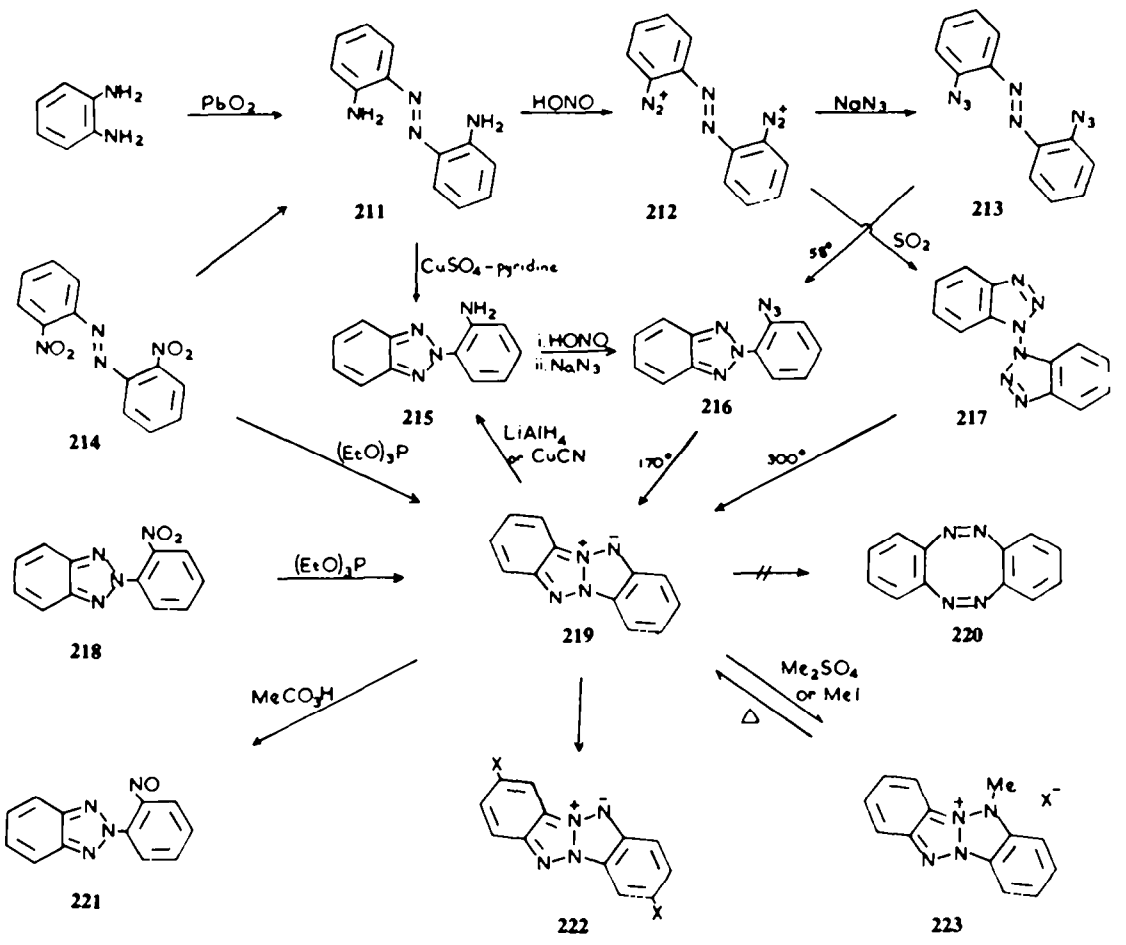
By employing the usual transformations of functional groups, the diesters (**206**; R^1 = Ph, $R^2 = CO_2Me$ and R^1 = Me, $R^2 = CO_2Et$) have been converted into a wide variety of derivatives[117-120]—including the unsubstituted derivative **206** (R^2 = H, R^1 = Me).[118] Bromination of this compound (Br_2/AcOH) gives the dibromo derivative (**206**; R^2 = Br, R^1 = Me)[118] and the structure of this product [and also that of the dirubidium salt (**206**; R^1 = Me, $R^2 = CO_2^- Rb^+$)] has been confirmed by a detailed X-ray study (Section VIII, A, c).[121-124] Compound **206** (R^2 = H, R^1 = Me) forms a picrate and a 1:1 adduct with silver nitrate.[118] Like the pyrazolo[1,2-*a*]-1,2,3-triazoles (**183**), the unsubstituted compound (**206**; R^2 = H, R^1 = Me) gives a formyl derivative (**206**; R^2 = CHO, R^1 = Me) under Vilsmeier-Haack conditions.[118]

Dibenzo derivatives of the tetraazapentalenes have been prepared by several routes and their chemistry has been studied in some detail.[126-133] The unsubstituted compound **219** (Scheme 9) is obtained[126] as yellow needles, m.p. 238°, and its structure has been confirmed by X-ray crystallography.[134] The preparation and chemistry of this compound (**219**) is summarised in Scheme 9.

Triethyl phosphite reduction of either 2,2'-dinitroazobenzene (**214**)[127,128] or *o* - nitrophenyl - 2H - benzotriazole (**218**)[128,131] gives the dibenzo*tetraaza*pentalene (**219**) in good yield (Scheme 9). These reactions can be regarded as proceeding via a nitrene intermediate and similar transformations have previously been described for the preparation of the dibenzo*triaza*pentalenes (**183**). A nitrene intermediate is probably also involved in the preparation of compound **219** by thermal decomposition of 2 - (*o* - azidophenyl) - 2H - benzotriazole **216** (Scheme 9).[129] This azide (**216**) has been prepared from 2,2'-diaminoazobenzene (**211**) by two routes (Scheme 9).[129] Another route to compound **219** involves the thermal decomposition of the 1,1'-dibenzotriazole (**217**), which is obtained by reduction of the diazonium salt (**212**) using sulphur dioxide (Scheme 9).[132]

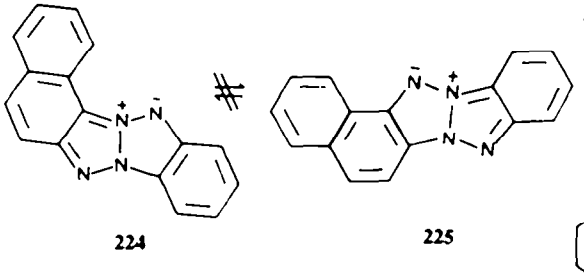
The dibenzo compound (**219**) is reduced to *o* - aminophenyl - 2H - benzotriazole (**215**) using either lithium aluminium hydride or cuprous cyanide.[130] Oxidative N-N bond cleavage is achieved using peracetic acid and the product is the nitroso compound **221** and/or its dimer.[130] Treatment of compound **219** with methyl iodide or dimethyl sulphate gives the N-Me salts (**223**) which revert to the mesomeric betaine (**219**) upon heating. The benzene rings of compound **219** undergo a number of facile electrophilic substitution reactions. The predominant product is commonly a disubstituted derivative of the type **222**. For example, treatment with chlorine or bromine in acetic acid gives the dihalo derivatives (**222**; X = Cl or Br) and nitration with 70% nitric acid gives mainly the dinitro compound (**222**; $X = NO_2$).[130]

The possibility that compound (**219**) undergoes a degenerate rearrangement via the valence tautomer (**220**) has been considered and eliminated.[129] The ^{1}H NMR spectrum of **219** is invariant over a wide range of tem-



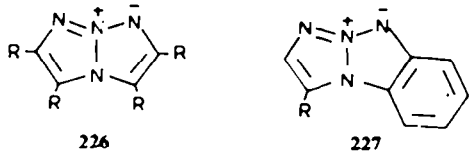
Scheme 9

perature.[129] Furthermore, the isomers **224** and **225** have been prepared and cannot be interconverted.[129]



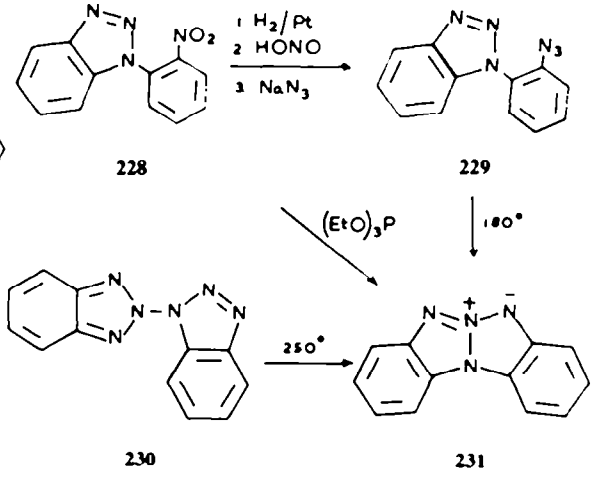
224 **225**

(D) 1,2,3 - *Triazolo*[1,2-a] - 1,2,3 - *triazoles* (**226**)



226 **227**

Dibenzo - 1,2,3 - triazolo[1,2-*a*] - 1,2,3 - triazoles (**231**) have been prepared[127,129,131,132,135] by methods directly analogous to those used to prepare the isomeric dibenzo systems (**219**). The preparative routes to the unsubstituted dibenzo system (**231**) are summarised in Scheme 10. Similar routes have been employed to prepare the monobenzo derivative (**227**; R = H).[127,131]



Scheme 10.

The dibenzo-tetraazapentalene (**231**) is similar to, but quite distinct from, the isomeric dibenzo system (**219**).[129] Compound **231** is obtained as colourless crystals m.p. 255° and has a dipole moment of 4.73 D whereas the isomer **219** has no detectable dipole moment and is obtained as yellow crystals, m.p. 238°.[129] Compound **231** undergoes Menchutkin methylation but the resulting salt is less stable than that formed by the isomer **219**.[131] The monobenzo deriva-

tive (227; R = H) is distinctly more reactive, readily forming an N-Me derivative with methyl iodide.[131]

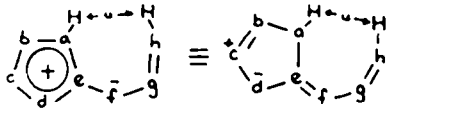
Like its isomer (219) the dibenzo system (231) readily undergoes electrophilic substitution on the benzene rings. In nitric acid, mononitro, dinitro or tetranitro derivatives are formed depending upon the acid concentration and the temperature.[131] Similarly, chlorine gives a dichloro derivative. The monobenzo derivative (227; R = H) is much more reactive towards electrophiles than the dibenzo compound (231). For example, compound (227; R = H) readily reacts with tetracyanoethylene initially giving a deep blue complex which then proceeds to lose hydrogen cyanide giving the tricyanovinyl derivative [227; R = $C(CN)C(CN)_2$].[131]

Precise heats of formation of the dibenzo isomers 219 and 231, and the corresponding monobenzo derivatives, have been determined.[136] The triazolo[1,2-*a*]triazoles (226) are found to be more stable than the triazolo[1,2-*b*]triazoles (206) by *ca.* 10 kcal/mole. Resonance energy considerations suggest that these molecules are aromatic in the usual thermodynamic sense.[136]

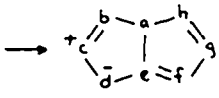
VI. HETEROPENTALENE MESOMERIC BETAINES OF TYPE C

Only recently has the preparation of a representative of the type C mesomeric betaines been reported.[137] However, the chemistry of this single derivative is of sufficient interest to justify the study of many more derivatives of this general structural type 39.

It is interesting to note the relationship between the type C mesomeric betaines (39) and the meso-ionic heterocycles (232).[6] The bicyclic structure 39 can be regarded as being formed by intramolecular *union* (←u→) of the meso-ionic structure 232. We do not wish to suggest that the mesomeric betaines (39) should be described or represented as meso-ionic compounds, but simply to indicate the relationship between these two types of mesomeric betaine (39 and 232).



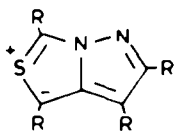
232 232



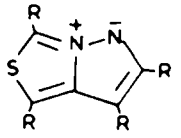
39

If the atoms or groups a, b, c, d, e, f, g and h in the general structure 39 (Table 3) are selected from suitably substituted C, N, O and S atoms, then 96 discrete structural types can be recognised. Since only a single representative is known, plenty of synthetic challenges and much interesting chemistry remain to be discovered in this field.

(A) *Pyrazolo*[2,3-c]*thiazoles* (233)

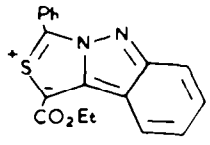


233a



233b

Maroon needles, m.p. 168–169°, identified as the monobenzo pyrazolo[2,3-*c*]thiazole (234) have been obtained in 24% yield by reductive cyclisation of the 4 - (*o* - nitrophenyl) - thiazole (235) using triethylphosphite.[137] This compound is the only known mesomeric betaine of type C; its structure is fully supported by its analytical and spectral properties and by its chemical reactions. A second product (5%) from this triethylphosphite deoxygenation has been shown to have the empirical formula $C_{18}H_{14}N_2O_2$ but, as yet, no constitutional formula has been assigned to this colourless product, m.p. 143°.[137]



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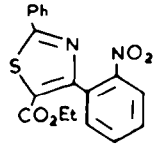
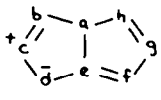


235

The pyrazolo[2,3-*c*]thiazoles (233) can be represented by two types of 1,3-dipolar structure. Written as 233a, the system resembles the type A mesomeric betaines (e.g. 89a) whereas written as 233b it resembles the type B mesomeric betaines (e.g. 179). One might expect, therefore, that in their chemical reactions the type C systems (233) would exhibit a mixture of type A and type B character. It was, therefore, of great interest to discover the general chemical behaviour of the pyrazolo[2,3-*c*]thiazole (234) and other type C systems.

As if realising that fate had chosen it as spokesman for its ninety-five undiscovered kindred, the pyrazolo[2,3-*c*]thiazole (234) dutifully rose to the occassion and demonstrated both type A and type B character.[137] With N-phenylmaleimide in boiling xylene, compound 234 underwent a 1,3-dipolar cycloaddition across the thiocarbonyl ylide dipole (e.g. 233a) giving the cycloadduct 236 (65%) or more correctly its enol 237, together with the pyrido[1,2-*b*]indazole-2,3-dicarboximide 238 (29%).[137]

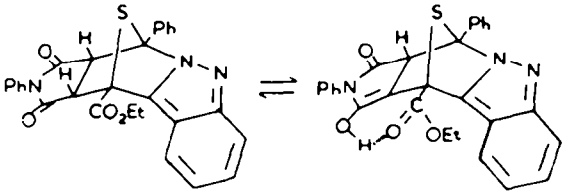
Table 3. Known mesomeric heteropentalenes of type C (39)



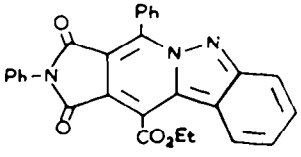
Parent system	Heterocycle	Atom or group[a] a	b	c	d	e	f	g	h
Pyrazolo[2,3-*c*]thiazoles	(233)	N	CR	S	CR	C	CR	CR	N

[a]The groupings a and c each contribute 2 electrons to the π-electron system of the heterocycle; b,d,e,f,g and h each contribute 1 electron.

The second product (**238**) is formed from the primary adduct (**237**) by thermal elimination of hydrogen sulphide and the yield of this product (**238**) increases with increasing reaction time. The transformation (**237** → **238**) also takes place upon treatment of the adduct (**237**) with methanolic sodium methoxide.[137] This type of 1,3-dipolar cycloaddition reaction (**234** → **237**) is typical of the type A mesomeric betaines (Section IV) and under these conditions the pyrazolo[2,3-*c*]thiazole (**234**) is clearly behaving like a type A system.

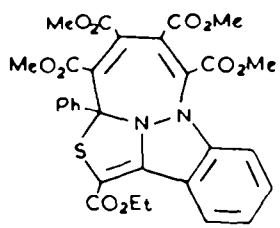


236 **237**



238

When dimethyl acetylenedicarboxylate was used as 1,3-dipolarophile, a different type of addition took place.[137] In this case, a 1:2 adduct having structure **239** was formed in 82% yield. Presumably an initial Michael addition gives the 1,4-dipolar intermediate (**240**) which reacts with a second molecule of the acetylene giving the product **239** whose structure is supported by its ^{13}C pulsed FT spectrum.[137] This reaction (**234** → **239**) is analogous to the reaction of pyrazolo[1,2-*a*]-1,2,3-triazoles (**179**) with dimethyl acetylenedicarboxylate (Section V, B) and in this reaction the pyrazolo[2,3-*c*]thiazole (**234**) is clearly behaving like a type B mesomeric betaine.



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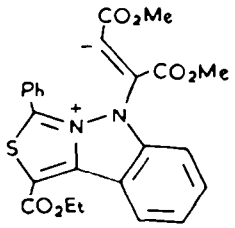
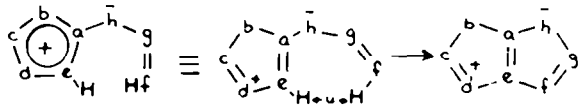


240

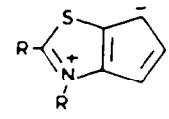
VII. HETEROPENTALENE MESOMERIC BETAINES OF TYPE D

Like the type C derivatives (**39**), the type D mesomeric betaines (**40**) are related to meso-ionic compounds (i.e. **241** → **40**) and only a single representative (Table 4) of the 96 possible structural types (**40**; b, d = O, NR, S; c, f, g, h = CR, N) has been reported.[33]

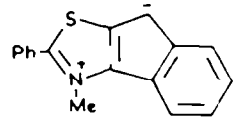


241 **241** **40**

(A) *Anhydro cyclopenta[d]thiazolium hydroxides* (**242**)



242



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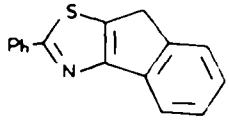

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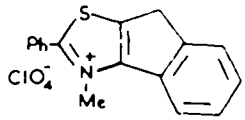


245

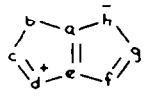
The monobenzo derivative (**243**) has been obtained as an unstable, purple solid by methylation of 2-phenylindeno[1,2-*d*]thiazole (**244**) and deprotonation of the resulting thiazolium perchlorate (**245**) with alkali.[33]

VIII. THE STRUCTURE, BONDING AND REACTIVITY OF HETEROPENTALENE MESOMERIC BETAINES

(A) *X-ray crystallography*

(a) *Thieno[3,4-c]thiophenes* (**89**) (Section IV, C). The molecular geometry of the thienothiophenes (**89**) is of some interest in connection with the question of the importance of sulphur *d*-orbitals in their bonding. The crystal structure of the tetraphenyl derivative (**246**) has been examined[61] and it was found that the thienothiophene nucleus is symmetrical and planar with the Ph groups rotated out of this plane by 39.6° and 58.4°. The average bond lengths in the bicyclic nucleus are as follows: CS, 1.706 Å; C_1C_2, 1.452 Å; $C_2C_{1'}$ 1.407 Å. Compared with thiophene, the CS bond length is slightly shorter (thiophene CS; 1.714 Å) whereas the CC bond

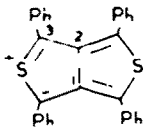
Table 4. Known mesomeric heteropentalenes of type D (**40**)



Parent system	Heterocycle	Atom of group[a] a	b	c	d	e	f	g	h
Anhydro cyclopenta[*d*] thiazolium hydroxides	(**242**)	C	NR	CR	S	C	CR	CR	CR

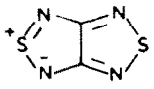
[a] The groupings b and d each contribute 2 electrons to the π-electron system of the heterocycle; a, c, e, f, g and h each contribute 1 electron.

lengths are substantially longer (thiophene CC; 1.370 Å and 1.423 Å). These changes in bond length relative to thiophene have been rationalised by invoking a contribution from the sulphur *d*-orbitals.[61]



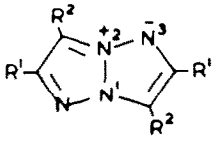
246

(b) 1,2,5 - *Thiadiazolo*[3,4-c] - 1,2,5 - *thiadiazole* (**159**) (Section IV, K). An X-ray study[81] has confirmed the planar structure of this molecule (**159**) and the bond lengths and bond angles are in accord with its symmetrical geometry (CC, 1.44 Å; NC, 1.35 Å; NS, 1.62 Å; NCC, 114.0°; CNS, 104.4°; NSN, 103.2°).



159

(c) 1,2,3 - *Triazolo*[1,2-b] - 1,2,3 - *triazoles* (**206**) (Section V, C). The crystal structures of four triazolotriazoles have been studied[121,125,134] including a preliminary examination[134] of the dibenzo derivative (**219**) which was shown to be planar. The structures of the rubidium salts **206** (R^1 = Me, R^2 = CO_2 Rb^+)[122,124,125] and **206** (R^1 = CO_2 Rb^+, R^2 = H)[121] have been studied in some detail and their geometry is entirely consistent with the proposed mesomeric betaine structures. Similar results were also found for the dibromo derivative (**206**; R^1 = Me, R^2 = Br)[123,125] in which the average bond lengths are as follows: N^1N^2, 1.36 Å; N^2N^3, 1.40 Å; N^2C, 1.40 Å; N^3C, 1.37 Å; CC, 1.33 Å.



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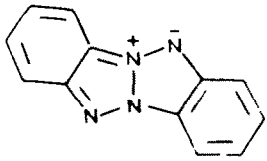
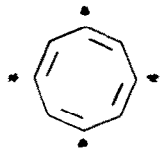


219

(B) *Electronic structure*

(a) *Qualitative aspects of the bonding in heteropentalene mesomeric betaines.* In order to discuss the electronic structure of the heteropentalene mesomeric betaines it is convenient first of all to consider the bonding in the cyclooctatetraene dianion (**248**), and isoelectronic heterocycles, and then to consider the heteropentalenes as perturbations of these systems.

Planar cyclooctatetraene (**247**) is an even alternant hydrocarbon (AH) and like all cyclic 4n polyenes it is characterised by a pair of non-bonding molecular orbitals (NBMO), each associated with one electron. The component C atoms can be divided into two sets, starred and unstarred, in such a way that no atoms of like parity are directly bonded. Since the NBMO's are degenerate eigenfunctions, any combinations of these molecular orbitals are also eigenfunctions and in fact it is possible and convenient to choose combinations such that one NBMO is restricted to all the starred atoms (e.g. **249**) and the other is restricted to the unstarred atoms (e.g. **250**). The introduction of two extra electrons into the NBMO's gives the well known cyclooctatetraene dianion (**248**).



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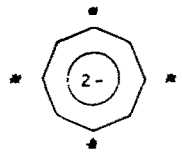

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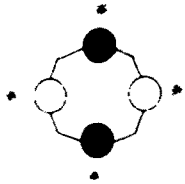

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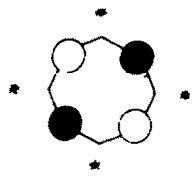
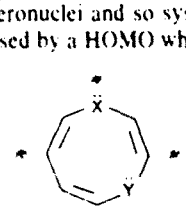


250

Let us now consider the consequences of introducing two hetero-lonepairs into the planar cyclooctatetraene (COT) skeleton in order to derive neutral heteroconjugated systems isoelectronic with the COT dianion. Classical structures for AH's are drawn by linking atoms of opposite parity by double bonds and the converse immediately follows: in order to be able to draw a classical structure there must be equal numbers of atoms of opposite parity. In the COT framework (**247**) there are four starred atoms and four unstarred atoms. If the lonepairs in an isoelectronic heterocycle originate at atoms of opposite parity, three starred and three unstarred atoms will remain, and it will be possible to represent heterocycles of this type by classical structures. This is clearly demonstrated by systems of the general type **251** and **252**. Furthermore, since one NBMO is associated with starred atoms and the other with unstarred atoms, both NBMO's will be perturbed by the heteronuclei in these systems (**251** and **252**) and they will be characterised by highest occupied molecular orbitals (HOMO) which are lower in energy than a NBMO.

If both the hetero-lonepairs originate at atoms of like parity, we can immediately predict that it will be impossible to represent these systems by classical structures. This prediction is illustrated by systems of the general type **253** and **254** which can only be represented as mesomeric betaines. It also follows that since the heteroatoms are restricted to one set of atoms (starred), only one of the NBMO's will be perturbed by the heteronuclei and so systems of this type will be characterised by a HOMO which is closely related to a NBMO.



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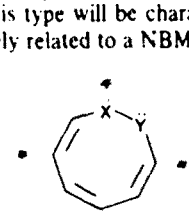

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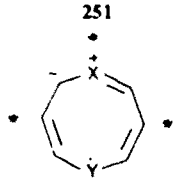
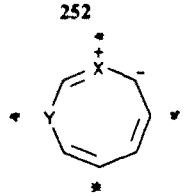


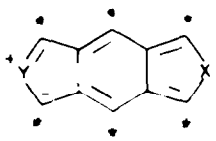
253



254

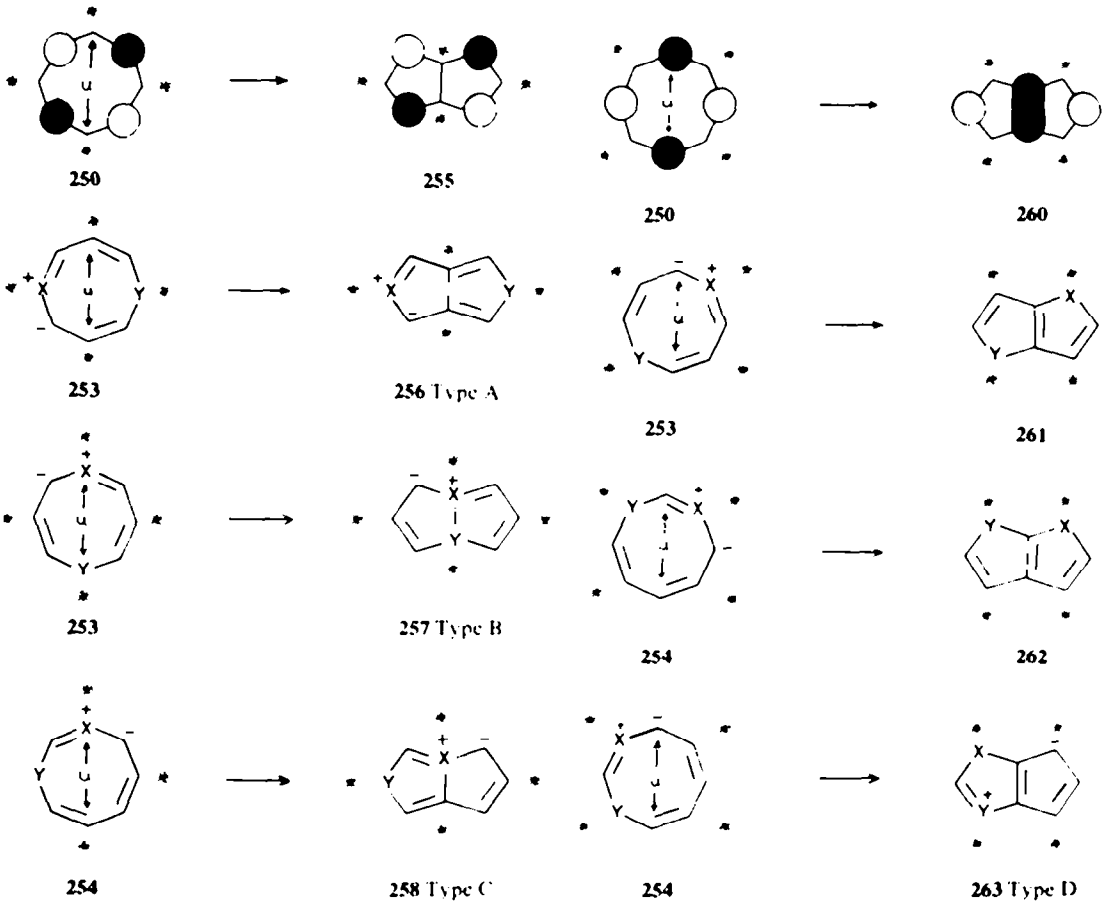
Mesomeric betaines of the general types **253** and **254** are not known but the relationship of these systems to heteropentalene mesomeric betaines is easy to demonstrate. In the heteroconjugated systems (**253** and **254**) the unperturbed NBMO (e.g. **250**) vanishes on the starred atoms and consequently an intramolecular union across starred atoms, e.g. (**250** → **255**), will leave the NBMO unchanged. Since the unstarred atoms are the major set of those atoms contributing a single electron, a simple consideration of the topology of the bicyclic systems (**256**, **257** and **258**) obtained by intramolecular union of **253** and **254** across starred positions demonstrates that they cannot be represented by a classical structure (i.e. it would be necessary to link at least one pair of unstarred atoms by a double bond, which is clearly impossible). Thus, we can quite generally conclude that the bicyclic heterosystems (**256**, **257** and **258**), which we now recognise as type A, B and C heteropentalene mesomeric betaines, cannot be represented by a classical structure and will be associated with a NBMO. This NBMO is an important feature of the structure of the type A, B and C mesomeric betaines and is closely related to their reactivity as 1,3-dipoles: a separate section is devoted to this aspect of their chemistry (Section VIII, C).

The analysis described above is easily extended to larger cyclic 4n polyenes and related polycyclic systems. For example, it can be similarly demonstrated that systems of the general type (**259**) can only be represented as mesomeric betaines and will be associated with a NBMO; other systems can be predicted.



259

Let us now return to the 8-membered cyclic mesomeric betaines of general structure **253** and **254** and consider the consequences of intramolecular union across *unstarred* atoms, e.g. **253** → **261**, **254** → **262** and **254** → **263**. Since the NBMO is finite and in phase at these positions, union results in a bonding interaction (i.e. **250** → **260**). The bicyclic systems (**261**, **262** and **263**) are not, therefore, associated with a NBMO; the HOMO will be lower in energy. Because union takes place across unstarred positions it is possible that the resulting systems can be represented by classical structures in which one double bond links unstarred atoms (the parent hydrocarbon is not alternant). In fact inspection of the structures **261**, **262** and **263** demonstrates that two of these systems, (**261** and **262**), are indeed satisfactorily represented by classical structures. The third system (**263**), which we now recognise as a type D heteropentalene mesomeric betaine, cannot be represented classically. Furthermore, we should now recognise that the type D heteropentalene mesomeric betaines (**263**), in that they are not associated with a NBMO, are fundamentally different from the type A, B and C heteropentalene mesomeric betaines (**256**, **257** and **258**). Thus, whereas the type A, B and C systems have many similarities in their chemical and spectroscopic properties, we might expect the type D systems to be rather different in character.



(b) *Semiempirical molecular orbital calculations.* Quantitative theoretical studies of heteropentalene mesomeric betaines have been made using the Hückel (HMO),[35,138,139] Pariser-Parr-Pople (PPP)[53,140,141] and CNDO/2[50,142] methods and the results are in good agreement with the qualitative analysis described above. The HMO method, in spite of being of doubtful validity for non-alternant hydrocarbons or heterosystems, provides useful insight into the π-bonding: as expected, type A, B and C molecules of general structure (256–258) are associated with non-bonding molecular orbitals. However, since the PPP and CNDO/2 approximations are sounder models for non-alternant heterosystems, only results obtained using these methods will be included in this section.

CNDO/2 calculations[142] for the nitrogen derivatives (**264–267**; Fig. 2) have been carried out and the calculated π-energy levels are as shown in Fig. 2. The geometries of the species **264–267** were based upon standard bond lengths and bond angles. Since the energy and symmetry of π molecular orbitals are fairly insensitive to small changes in molecular geometry, the results (Fig. 2) should provide a reasonable picture of the π-bonding in these systems. Figure 2 clearly demonstrates the electronic similarities of the type A, B and C systems (**264–266**). Each of these systems (**264–266**) is associated with a HOMO which is non-bonding in character (*ca.* −8.1 eV) and it is interesting to note that the type C system (**266**) has energy levels intermediate between those of the type A (**264**) and type B (**265**) systems. This latter observation provides another demonstration of the hybrid character of the type C systems. Figure 2 also clearly demonstrates that the electronic structure of the type D system (**267**) is fundamentally different to that of the mesomeric betaines (**264–266**); the HOMO of the type D molecule (**267**) is substantially lower in energy and is topologically different to that of the type A, B and C molecules.

Since the HOMO of the type A, B and C systems (**256–258**) vanishes at starred positions, the energy of this molecular orbital might be expected to be insensitive to changes in the nature of atoms at these positions. This is

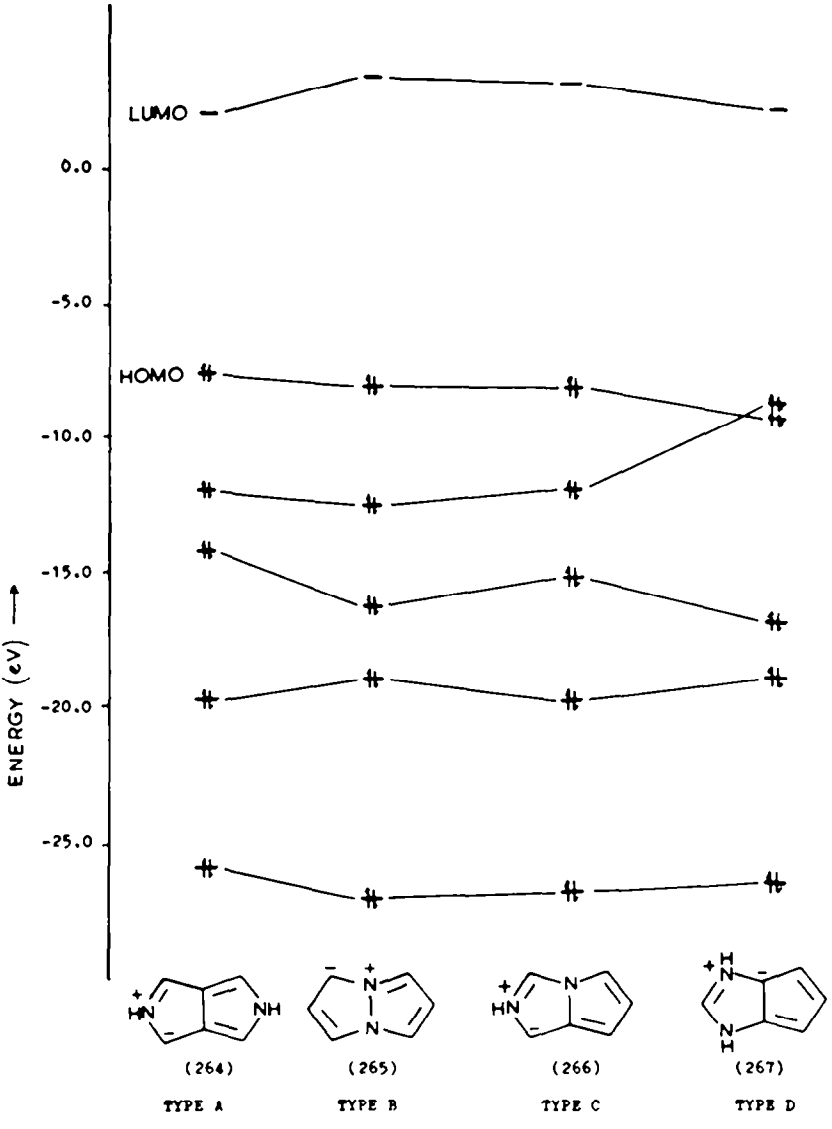


Fig. 2. The energy levels of π-electrons in heteropentalene mesomeric betaines calculated by the CNDO/2 method.

not the case for the unstarred positions of the heteropentalene skeletons (**256–258**) and it is of interest to consider the effect of substituting N atoms at these positions. Using the CNDO/2 method, this heteroatom effect has been investigated for the type A species (**268–272**; Table 5) and the results are shown in Table 5.[142] Introduction of N atoms results in a progressive lowering of the energy of the HOMO and this perturbation can be expected to have a marked influence on the reactivity of type A systems with 1,3-dipolarophiles (Section VIII, C).

The calculated effect of heteroatoms on the HOMO-LUMO splitting of the type A systems (Table 5) is also informative. Increasing the number of N atoms (**268–272**) results in a small but progressive increase in the HOMO-LUMO separation. This effect is reflected in the colour of type A molecules. Those systems associated with C atoms at unstarred positions (e.g. **256**) are highly coloured undoubtedly due to a HOMO-LUMO transition. Typical examples (Table 6) are the *purple* thieno[3,4-*c*]thiophene (**273**) and the *red* thieno[3,4-*c*]pyrrole (**274**). Introduction of N atoms results in a shift of the visible absorption band to shorter wavelengths. Thus, the thieno[3,4-*c*]pyrazole (**275**) is *orange*, the pyrazolo[4,3-*c*]pyrazole (**276**) is pale *yellow* and ultimately the triazolo[4,5-*d*]triazole (**277**) is *colourless*.

CNDO/2[50] and PPP[53,140,141] calculations on sulphur systems have been reported. Results using the PPP method suggest that the thieno[3,4-*c*]thiophene (**278**)[140,141] and the thieno[3,4-*c*]pyrrole (**279**)[53] systems should be considerably less stable than classical isomers. In fact these calculations predicted that the unsubstituted systems (**278** and **279**) should have a triplet ground state.

Table 5. The influence of heteroatoms on the HOMO and LUMO of type A heteropentalenes calculated by the CNDO/2 method

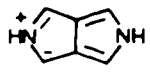
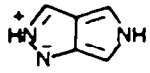
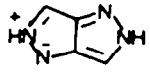
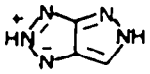
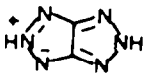
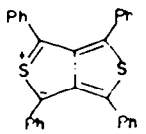
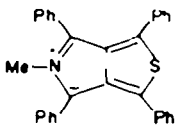
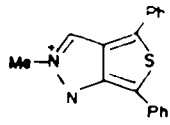
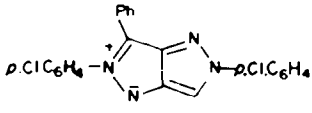
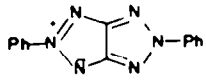
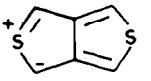
Molecule		HOMO (eV)	HOMO-LUMO Separation (eV)
	**268**	7.6	9.95
	**269**	−8.4	10.04
	**270**	−9.0	10.05
	**271**	−9.5	10.07
	**272**	10.1	10.06

Table 6. The effect of heteroatoms on the visible absorption of type A heteropentalene mesomeric betaines

Molecule		Appearance	λ_{max} (nm)	Solvent
	**273**	purple needles	551 (log ϵ3.92)[51]	$CHCl_3$
	**274**	red needles	533 (log ϵ3.15)[51]	$CHCl_3$
	**275**	orange prisms	465 (log ϵ4.44)[63]	MeOH
	**276**	pale yellow crystals	398 (log ϵ4.33)[65]	$CHCl_3$
	**277**	colourless leaflets	342 (log ϵ4.60)[78]	EtOH

although subsequently spectroscopic studies on derivatives of **278** and **279** have demonstrated a singlet ground state. This discrepancy between calculated and observed properties may possibly be attributable either to the neglect of *d*-orbitals in these calculations or to the influence of phenyl substituents in the experimental studies.

Cava *et al.*[50] have employed the CNDO/2 method with inclusion of sulphur *d*-orbitals to investigate the structure of the sulphur heterocycles (**278**, **279** and **280**). The results of this study are consistent with the view that *d*-orbitals make a significant contribution to the π-bonding. In particular, a substantial part of the π-bonding between carbon and sulphur was attributable to $d\pi - p\pi$ overlap.



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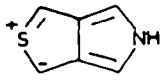

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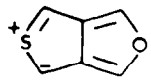

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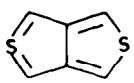

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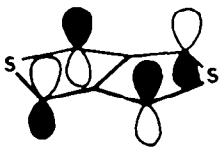
(c) d-*Orbital participation*. The question of the extent of the participation of sulphur *d*-orbitals in the bonding of heteroaromatic systems is a vexing one. It has been suggested that sulphur 3*d*-orbitals make an important contribution to the bonding of thieno[3,4-*c*]thiophenes (**89**) and related heteropentalene mesomeric betaines (**69**, **85**, **107**, **139**, **156**, **159** and **163**)[14,143,144] but a critical, quantitative assessment of the extent of this contribution is not yet available. In the opinion of the author, an understanding of this interesting aspect of sulphur chemistry will be gained by a comparison of spectroscopic properties of a wide variety of structural types; the value of molecular orbital studies in these investigations is questionable since these models often beg the question. Cava and Lakshmikantham[14] have succinctly summarised the current situation regarding the nature of the sulphur bonding in these systems: "*further insight into this problem will best be gained . . . not by polemics but by new experimental work.*" A qualitative analysis of the factors governing the role of *d*-orbitals is included here but it would be premature to attempt a definitive appraisal.

In a valence bond description, the participation of sulphur *d*-orbitals in the bonding of thieno[3,4-*c*]thiophenes (**89**) is included by assuming that canonical forms of the type **281** make a significant contribution. Alternatively, in a molecular orbital treatment *d*-orbital participation arises from a mixing of the NBMO of the heteropentalene framework (e.g. **282**) with a combination of the topologically favourable sulphur d_{yz} orbitals (e.g. **283**); weaker interactions may also arise between the sulphur d_{xz} orbitals and suitable π molecular orbitals but these are of secondary importance. For quantitative studies of the importance of *d*-orbitals, this molecular orbital picture provides an attractive model and the whole question of the factors influencing the contribution of 3*d*-orbitals can be directed to those factors which govern d_{yz}-NBMO mixing (Fig. 3).

If the introduction of sulphur *d*-orbitals is considered as a perturbation in the bonding of heteropentalenes, then in accord with second order perturbation theory the



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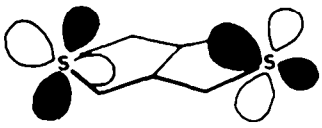

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extent of mixing of the component orbitals (NBMO and d_{yz}) is inversely proportional to their difference in energy (ΔE; Fig. 3) and is dependent on their overlap. Undoubtedly, the NBMO is very favourable for interaction with sulphur d_{yz} orbitals, being high in energy and having suitable symmetry. The problem, therefore, lies with the sulphur *d*-orbitals themselves. Are they of low enough energy and is the overlap integral with the NBMO large enough for them to make a significant contribution to the π-bonding?

Participation of *d*-orbitals certainly seems to be important in systems where the sulphur atom is associated with a positive charge (e.g. sulphur ylides)[145-147] or is directly bonded to electronegative elements (e.g. SF_6).[148] In such molecules the charge associated with the sulphur atom appears to result in a lowering of the *d*-orbital energy as well as a contraction of the orbital size making overlap more effective. However, in systems where the S atom is associated with little or no charge the suitability of the *d*-orbitals for bonding interactions is not clear. Admittedly, $d\pi - p\pi$ bonding appears to stabilise dithiane anions (R–SCHS–R) but in these systems the carbanionoid orbital is extremely high in energy and $d\pi - p\pi$ overlap is good. It could be argued that sulphur *d*-orbitals are particularly important in the bonding of 1,2,5 - thiadiazolo[3,4-*c*] - 1,2,5 - thiadiazole (**159**) due to the effect of electronegative nitrogen atoms but these atoms will also have the effect of making the HOMO substantially lower in energy than a NBMO.

In conclusion, perhaps the following point is worth including. There is no law of nature which requires that molecules be represented by purely covalent structures. The observation that without inclusion of *d*-orbitals the thieno[3,4-*c*]thiophenes can only be represented as mesomeric betaines (**278**) is not sufficient justification, without other evidence, for invoking *d*-orbital participation. Indeed, the preparation of pyrazolo[4,3-*c*]pyrazoles (**117**) and 1,2,3 - triazolo[4,5-*d*] - 1,2,3 - triazoles (**146**) demonstrates that *d*-orbitals are not essential for the

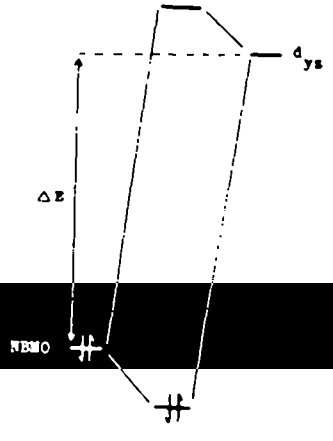


Fig. 3. The mixing of sulphur d_{yz} orbitals and a NBMO in the π-bonding of heteropentalene mesomeric betaines.

stability of type A heteropentalene mesomeric betaines (37). Undoubtedly *d*-orbitals are involved in the bonding of the thieno[3,4-*c*]thiophenes (278) and related sulphur heterocycles but whether their contribution is large enough to significantly influence their structure and reactivity or to justify their representation by structures of the type 281 remains to be seen.

(C) 1,3-*Dipolar cycloaddition reactions*

The structural features and orbital topology of the heteropentalene mesomeric betaines provide the opportunity for 1,3-dipolar cycloaddition reactions which lead to novel structural types. These cycloaddition reactions have been discussed in previous sections but it is informative to examine the general factors which govern the reactivity and selectivity. Two factors seem to be of primary importance: (i) the energy and symmetry of the HOMO of the heteropentalene; (ii) the thermodynamic stability of the cycloadduct. Frontier molecular orbital (FMO) theory[149,150] has been successful in accounting for the reactivity of 1,3-dipolar systems in terms of HOMO-LUMO interactions and it is instructive to consider the cycloaddition reactions of the heteropentalene mesomeric betaines in these terms.

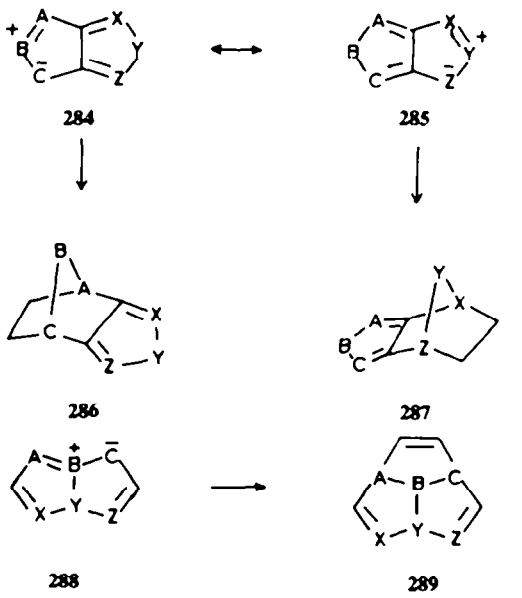
The reactivities of the mesomeric betaines (high energy HOMO) with electron deficient dipolarophiles (low energy LUMO) are controlled by the magnitude of the interaction between the mesomeric betaine HOMO and the dipolarophile LUMO.[150,151] The magnitude of this orbital interaction is inversely proportional to the energy difference and dependent on the orbital overlap, and in this connection it is significant that the HOMO's of the type A, B and C heteropentalene mesomeric betaines have nodal properties (255) suitable for overlap with antibonding orbitals of dipolarophiles. Large interactions between the frontier orbitals are expected to facilitate 1,3-dipolar cycloadditions.

This dependence of reactivity upon the energy and topology of the mesomeric betaine HOMO is demonstrated by the reactions of type A systems. Thus, the thieno[3,4-*c*]pyrroles (69), the thieno[3,4-*c*]furans (85) and the thieno[3,4-*c*]thiophenes (89), in which the HOMO is closely related to NBMO, react readily with electron deficient alkenes and alkynes, and a similar reactivity is observed for the thieno[3,4-*c*]pyrazoles (107). CNDO/2 calculations[142] (Section VIII, B, b) indicate that the introduction of N atoms into the bicyclic framework (Table 5) progressively lowers the energy of the HOMO and this is reflected in the chemistry of aza derivatives. In the thieno[3,4-*c*]thiadiazole system (139), where two nitrogen atoms perturb the HOMO, cycloaddition is "*sluggish*"[75] and the tetra-azapentalenes (pyrazolo[4,3-*c*]pyrazoles) (117) and the hexa-azapentalenes (triazolo[4,5-*c*]triazoles) (146) do not appear to show any 1,3-dipolar reactivity.

Some caution must be taken in assigning lack of 1,3-dipolar reactivity to the nature of the HOMO since the thermodynamic stability of the adduct is also an influential factor. This thermodynamic control may well account for the mode of addition to those type A systems which are associated with two discrete 1,3-dipolar fragments (e.g. 284↔285). Thus, the thieno[3,4-*c*]furans (85) and the thieno[3,4-*c*]pyrazoles (107) react as carbonyl ylides (85a) and thiocarbonyl ylides (107b) respectively although, in principle, alternative modes of addition are possible. The factors which govern the relative thermodynamic stability of isomeric adducts (e.g. 286 and 287) are not clear, however. Particularly amusing systems are the thieno[3,4-*c*]pyrroles (69) which with olefines react either as azomethine ylides (69a) or thiocarbonyl ylides (69b) depending upon the reaction conditions. Thus, in low boiling solvents, such as benzene, addition occurs across the azomethine ylide fragment. This mode of reaction is attributable to kinetic control of the product, the governing factor being the relative magnitude of the HOMO coefficients at the two alternative reaction centres. With higher boiling solvents, such as toluene, addition takes place across the thiocarbonyl ylide; a process which is clearly thermodynamically controlled although it would be difficult to predict this result *a priori*.

Type B and type C systems have also been demonstrated to participate in 1,3-dipolar cycloaddition reactions and the controlling factors seem to be essentially those described above. In the type B series, the pyrazolo[1,2-*a*]pyrazoles (164) and the pyrazolo[1,2-*a*]triazoles (179) react with acetylenes giving tricyclic adducts of the general type 289 although it is conceivable that some of these reactions (288→289) may proceed via a dipolar intermediate rather than a truly concerted mechanism. Considering the rigidity and apparently strained nature of the adducts (289), it is remarkable that the type B systems react in this manner at all.

This thermodynamic factor is almost certainly decisive in controlling cycloadditions of the type C heteropentalene mesomeric betaines where addition resembling the type A mode rather than the type B mode is favoured.



IX. CONCLUSION

The heteropentalene mesomeric betaines are intrinsically interesting molecules, particularly from the point of view of their electronic structure and their participation in 1,3-dipolar cycloaddition reactions. Numerous possible examples of this type of bicyclic species are still unknown and the existence of many novel tricyclic and polycyclic mesomeric betaines can also be predicted. It is hoped that future attempts to prepare new systems will be rewarding and that a study of their physical and chemical properties will enrich the organic chemists' concepts of bonding in heterocyclic systems as well as providing novel synthetic transformations.

It is intended that this review and a recent review of meso-ionic compounds[6] be parts of a trilogy covering the chemistry of heterocyclic mesomeric betaines. In the third article it is hoped to complete this survey by discussing the chemistry of the general class of mesomeric betaines which are isoelectronic with odd alternant hydrocarbon anions.[152]

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X. APPENDIX ADDED IN PROOF

This appendix extends the literature coverage to September 1977. Representatives of two new type A heteropentalene betaines systems have been reported; their structures are given in Table A-1. Section headings are used to facilitate direct reference to the main text. New headings are used for new classes of compound.

A comprehensive review of the chemistry of heteropentalenes having bridgehead nitrogen atoms is to be published.[153]

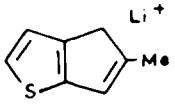
Table A-1. Appendix to Table 1

Parent system	Heterocycle	Atom or group							
		a	b	c	d	e	f	g	h
Thieno[3,4-*c*]isothiazoles	(291)	C	N	S	CR	C	CR	S	CR
Selenolo[3,4-*c*]selenophenes	(296)	C	CR	Se	CR	C	CR	Se	CR

SECTION II

(A) *Monoanions*

The isolation and characterisation of the lithium salt of the 5-methyl-1-thiapentalenyl anion (**290**) has been reported.[154]



290

SECTION IV

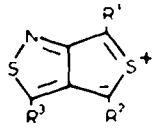
(B) *Thieno*[3,4-c]*furans* (**85**)

Base catalysed dehydration of the sulphoxide (**86**) apparently gives compound (**85**; $R^1 = R^2 = R^3 = R^4 = Ph$) in solution. This provides an alternative to dehydration using acetic anhydride.[155]

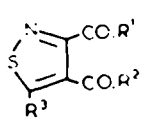
(C) *Thieno*[3,4-c]*thiophenes* (**89**)

A useful alternative to acetic anhydride catalysed dehydration of the sulphoxides (**90**) to the betaines (**89**) is a novel base catalysed dehydration in benzene solution. Grignard reagents and methyl lithium give low yields but lithium diisopropylamide or aqueous sodium hydroxide and phase transfer catalyst give good yields.[155]

(M) *Thieno*[3,4-c]*isothiazoles* (**291**)



291 See Table A-1



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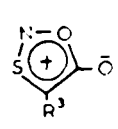

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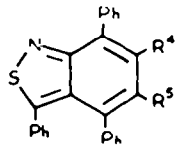

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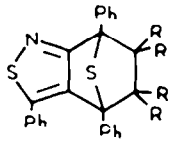
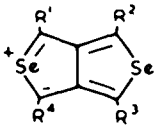


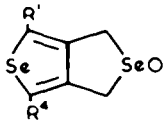
295

Violet needles ($\lambda_{max}^{CH_2Cl_2}$ 529 nm) of the triphenyl derivative (**291**; $R^1 = R^2 = R^3 = Ph$) have been prepared by 1, 3-dipolar cycloaddition of dibenzoylacetylene to the meso-ionic 1,3,2-oxathiazol-5-one (**293**; $R^3 = Ph$) and treatment of the resulting 3,4-dibenzoyl-5-phenylisothiazole (**292**; $R^1 = R^2 = R^3 = Ph$) with phosphorus pentasulphide-pyridine. Acetylenes add to compound (**291**; $R^1 = R^2 = R^3 = Ph$) across the thiocarbonyl ylide fragment giving benzo[*c*]isothiazole derivatives (**294**) without isolation of the intermediate primary adducts. With alkenes the primary adducts (**295**) are stable and can be isolated.[156]

(N) *Selenolo*[3,4-c]*selenophene* (**296**)



296 See Table A-1



297

Dehydration of the selenoxides (**297**) gives the selenolo[3,4-*c*]selenophenes (**296**; $R^1 = R^4 = Me$, CO_2Et, $R^2 = R^3 = H$) in solution but isolation of these species has not been achieved. These species (**296**) can apparently be trapped as their *N*-phenylmaleimide adducts.[157]

SECTION V

(A) *Pyrazolo*[1,2-a]*pyrazoles* (**164**)

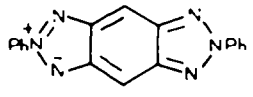
New dibenzo[*b,f*][1, 5] diazocine derivatives (**175**) have been reported.[158-160]

(D) 1,2,3-*Triazolo*[1,2-a]-*triazoles* (**226**)

The NMR spectrum of the dibenzo derivative (**231**) has been recorded and analysed.[161]

SECTION VIII (B)

(a) *Qualitative aspects of the bonding in heteropentalene mesomeric betaines.* In connection with systems of the general type (**259**) it is interesting to note that the tricyclic system (**298**) appears to have been prepared many years ago by oxidation of the *m*-phenylenediamine derivative (**299**) using cupric sulphate in pyridine.[162]



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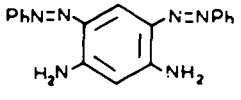

299

(b) *Semiempirical molecular orbital calculations.* Further examples of PPP and CNDO/2 MO calculations on pyrazolo[1,2-*a*]pyrazoles (**164**) and 1,2,3-triazolo[1,2-*b*]-1,2,3-triazoles (**206**) have come to the author's attention.[163-166]

(c) *d-Orbital participation.* An important study of the electronic structure of the thieno[3,4-*c*]thiophenes (**89**) employing the CNDO/S method and the photoelectron spectrum of the tetraphenyl derivative (**89**; $R^1 = R^2 = R^3 = R^4 = Ph$) has been reported. The high energy of the HOMO is demonstrated. It is concluded that these species are aromatic like thiophene and that *d*-orbitals do not play an important part in their bonding.[167]