# Heterocycles by Cycloaddition. Part 9.[1,2] Bridged Heteroannulenes by Cycloaddition–Extrusion–Ring-expansion Reactions of Mesoionic Compounds with Benzocyclopropene. A Methanothiazonine, a Methanothionine, and a Methanothiecinone

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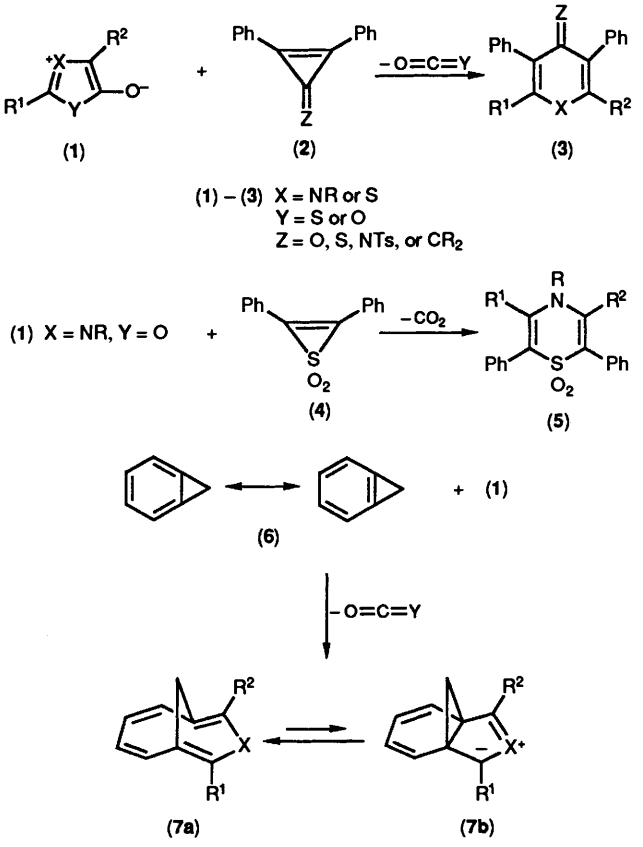
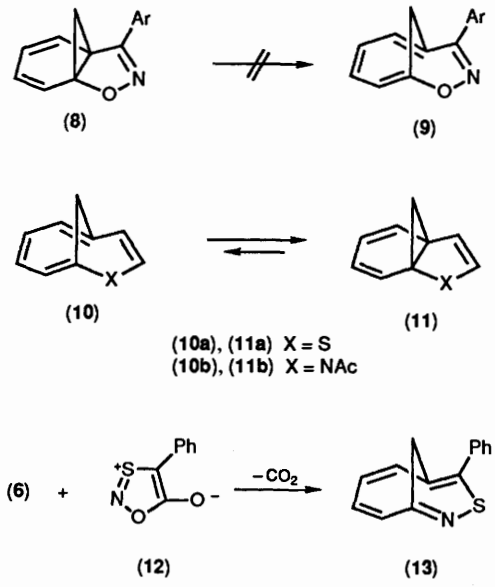
A methanothiazonine (**13**) was formed by cycloaddition–extrusion–ring expansion of benzocyclopropene with a mesoionic oxathiazoliumolate (**12**). The reaction with a dithioliumolate (**14**) gave the cycloadduct (**15**), from which a methanothionine (**16**) and a methanothiecinone (**19**) were prepared. Attempts at similar reactions with several other mesoionic systems failed to give the cycloadducts, or the cycloadducts did not form the desired extrusion products. The methanothionine (**16**) isomerised thermally to a cyclohepta[*c*]thiophene (**17**). The degree of electron delocalisation of these bridged annulenes is discussed.

As part of our programme to extend the use of mesoionic compounds as building blocks for heterocycles, we have reported the cycloaddition–extrusion–ring-expansion reactions of several mesoionic ring systems (**1**) with cyclopropene derivatives (**2**)[3] and a thiirene dioxide (**4**)[4] to give a variety of six-membered heterocycles (**3**) and (**5**). We thought it worthwhile to find out whether or not mesoionic compounds can react analogously with benzocyclopropene (**6**) which, though strained, is a system with a considerable degree of electron delocalisation.[5] If successful, these reactions would give bridged hetero[9]annulenes (**7a**) with 10 π-electrons over the conjugated system. If the expected cycloaddition takes place with an *exo* stereochemistry, then these reactions may be thought of as the first examples of a formal [6 + 4]π-cycloaddition of mesoionic compounds.[6] Carbocyclic bridged [10]annulenes[7] and their aza-analogues[8] have been well documented, but reports on 10 π-nine-membered heteroannulenes are relatively rare. Monocyclic azonines and an oxonine were prepared by Anastassiou.[9] It has been shown that the aromaticity of these systems varies considerably depending on the heteroatoms and the substituents, and that they isomerise more or less readily into bicyclic systems. Dibenzo-oxonine and dibenzothionine have been prepared and isolated.[10] There have been several attempted preparations of bridged heteronines. Nitta *et al.*[11] obtained the cycloadducts (**8**) of benzonitrile oxides with benzocyclopropene, but the cycloadducts could not be isomerised to the methano-oxazonine (**9**) (Scheme 1). After our preliminary reports,[2] Okazaki *et al.*[12] reported the successful preparation of unsubstituted 2,7-methanothionine (**10a**) and *N*-acetyl-2,7-methanoazonine (**10b**). However, it was found that the equilibrium of these systems is shifted far to the tricyclic norcaradiene isomers (**11**). From these results, it may be assumed that when a heteroatom which is capable of providing a pair of electrons takes a position adjacent to the bridgehead atom of a methanoheteronine, such a molecule preferentially takes the more stable tricyclic norcaradiene isomeric form. Isomerisation to the tricyclic valence isomers (**7b**) will be forbidden with the 3,8-methanoheteronines (**7a**). Vogel and coworkers tried to prepare the unsubstituted 3,8-methanothionine (**7a**; X = S, $R^1$ = $R^2$ = H) by dehydration of 1,3-dihydro-3a,7a-methanobenzo[*c*]thiophene *S*-oxide, but with unrewarding results.[13]




## Results and Discussion

*Synthesis.*—The reaction of the mesoionic 4-phenyl-1,3,2-oxathiazolium-5-olate (**12**)[14] with benzocyclopropene in benzene at room temperature slowly gave a main product. Spectral data (see Experimental section) of this product were in good agreement with the methanothiazonine (9-phenyl-8-thia-7-




**Scheme 1.**

azabicyclo[4.3.1]deca-2,4,6,9-tetraene) (**13**). Monitoring of this reaction by NMR spectroscopy showed that the yield of this compound reached a peak (32%) after 3 weeks at room temperature in deuteriochloroform, and then decreased gradually afterwards. However, attempted isolation of this product either by chromatography or low-temperature recrystallisation failed, and it darkened readily to give polymeric substances. Attempted isolation of a cycloadduct of this substance with dimethyl acetylenedicarboxylate (DMAD) was unsuccessful. The above results thus suggested that the desired reactions would occur by choice of an appropriate mesoionic system, but that the methanoheteronines are rather unstable, and the main reaction tends to become complex by secondary reactions when the cycloaddition and the extrusion–ring-expansion steps take place simultaneously under the reaction conditions.

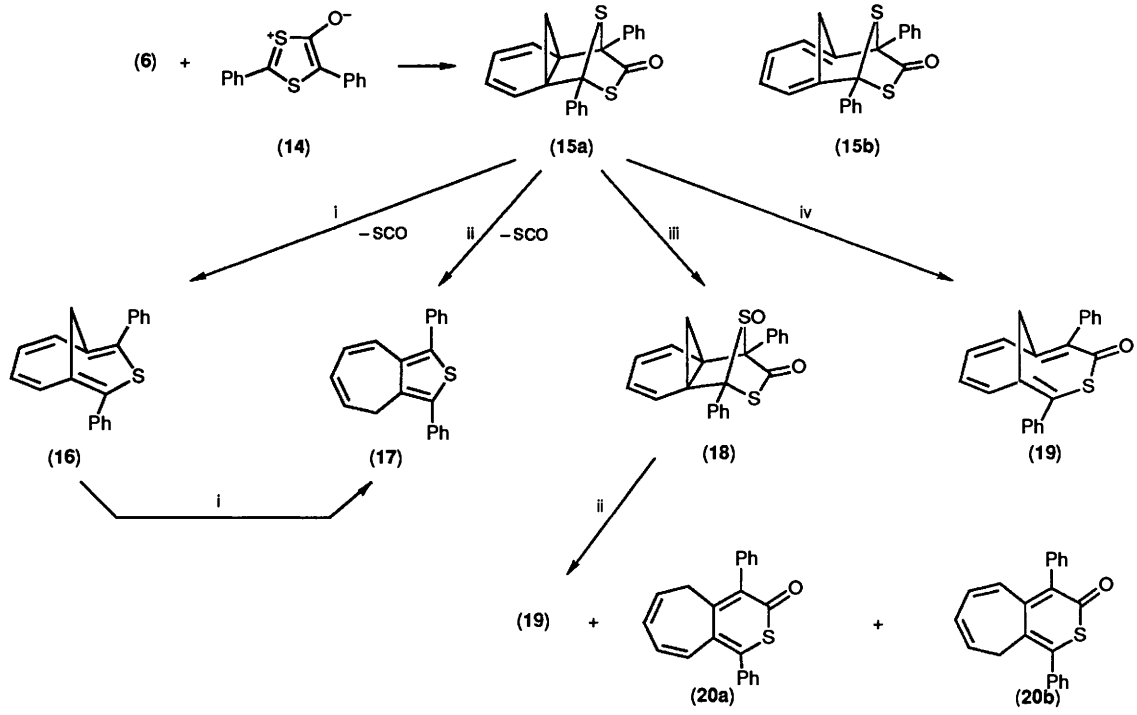
Based on these considerations, the reaction with the mesoionic 2,5-diphenyl-1,3-dithiolium-4-olate (**14**)[15] was tried next, because the cycloadducts of dithioliumolates with alkenes are generally stable. The reaction of the dithioliumolate (**14**) with benzocyclopropene at room temperature or under slight warming allowed isolation of the cycloadduct (**15**) in reasonable yield. The methylene and episulphide groups probably had the *syn*-configuration because the sulphur atom as well as the sulphoxide bridge (*vide infra*) exerted a large effect on the NMR spectral peaks of the methylene protons. If this assignment of configuration is correct, this result shows that the benzene plane (6π) prefers to approach from the direction which is *exo* to the plane of the thiocarbonyl ylide (4π) portion of the dithioliumolate. Measurement with $Eu(fod)_3$* showed that the proton which is *syn* to the sulphur atom is more strongly deshielded ($\delta_H$ 3.58). Both the $^{13}C$ chemical shift ($\delta_C$ 14.3) and coupling constants [$J^{(^{13}C-^{1}H)}$ 169 and 163 Hz and $J^{(^{1}H-^{1}H)}$ 5.3 Hz] showed that the adduct takes the tricyclic norcaradiene structure (**15a**) rather than the tropylidene isomeric form (**15b**). The electron-impact mass spectrum of the adduct (**15a**) showed only a very weak molecular-ion peak and the base peak corresponded to ($M^+$ − SCO), suggesting that carbonyl sulphide would be extruded readily from the cycloadduct (**15a**). When the cycloadduct (**15a**) was heated briefly in xylene, the expected diphenylmethanothionine (7,9-diphenyl-8-thiabicyclo[4.3.1]-deca-2,4,6,9-tetraene) (**16**) could be isolated. Once purified, the methanothionine (**16**) was relatively stable and could be stored for months when kept cooled with exclusion of air and moisture.

If the sulphur atom could be extruded from the cycloadduct (**15a**), a methanothiecinone (**19**) would be expected to be formed. This system may show a quasi-aromatic character by polarisation of the carbonyl group and delocalisation of the remaining 10 π-electrons. It was found earlier that carbonyl sulphide and sulphur respectively are selectively extruded by thermolysis and photolysis of the cycloadduct of a mesoionic dithioliumolate and benzyne.[16] Irradiation of the cycloadduct (**15a**) resulted in extrusion of carbonyl sulphide, and this was accompanied by a skeletal isomerisation to afford the cyloheptа-[*c*]thiophene (**17**). The adduct (**15a**) was converted into the corresponding sulphoxide (**18**) by treatment with *m*-chloroperbenzoic acid (MCPBA). Although the base mass spectral peak corresponded to extrusion of SO from the molecular ion, the sulphoxide was thermally stable. Photolysis of the sulphoxide (**18**) in benzene afforded the desired methanothiecinone (2,5-diphenyl-3-thiabicyclo[4.4.1]undeca-1,5,7,9-tetraen-4-one) (**19**) but only in low yield. The main products from this reaction were the two cycloheptathiopyranone isomers (**20a**) and (**20b**). It was later found that the methanothiecinone (**19**) is formed almost quantitatively by desulphurisation of the cycloadduct (**15a**) with tributylphosphine (Scheme 2).

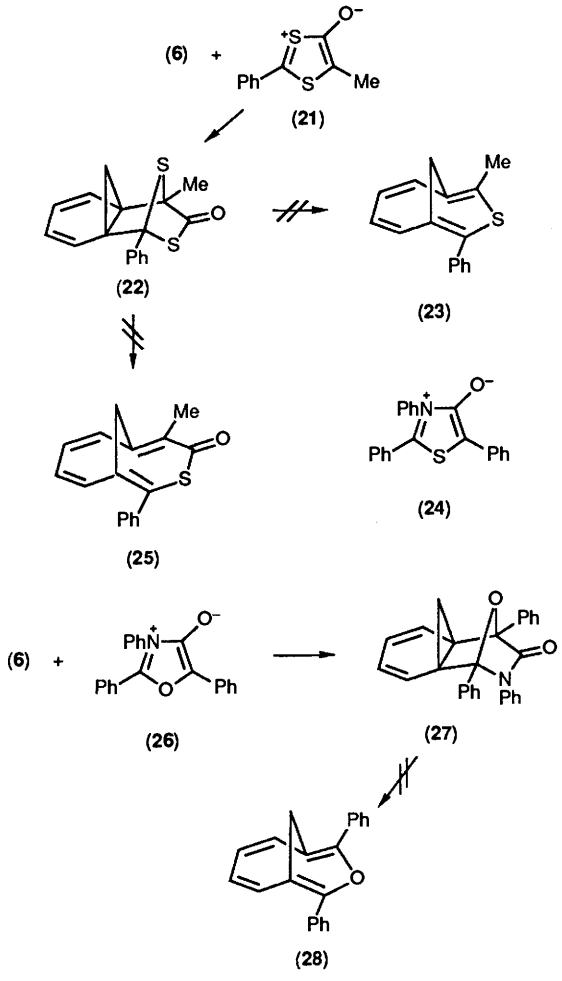
*Scope and Limitation.*—From the results described above, it may appear that the reactions of this type should allow preparation of a large variety of such bridged heteronines because several mesoionic systems with various heteroatoms at various positions are known. It soon became clear that the generality of the reactions of this type is poor. The preparation of 2-methyl-9-phenyl-3,8-methanothionine (**23**) was attempted in order to evaluate the magnetic effect exerted by the phenyl substituents. The potential precursor (**22**) could be formed in low yield from the mesoionic 5-methyl-2-phenyldithiolium-4-olate (**21**).[15] Replacement of only one of the two phenyl groups of compound (**14**) by a methyl group [in mesoionic (**21**)] provided a high thermal stability to the adduct (**22**), and complex products resulted from forced pyrolysis. Equally unsuccessful were attempted preparations of the methanothiecinone (**25**) by elimination of the sulphur atom from the adduct (**22**) by treatment with tributylphosphine, dichlorocarbene [from phenyl(trichloromethyl)mercury], or sodium amalgam. The mesoionic triphenylthiazolium-4-olate (**24**)[17] did not react with benzocyclopropene.

In an attempt to prepare a methano-oxonine (**28**), the cycloadduct (**27**) of the mesoionic triphenyloxazolium-4-olate (**26**) and benzocyclopropene was prepared in an acceptable yield (Scheme 3). The oxazolium-4-olate (**26**) was prepared by a modification of Haddadin's method[18] (see Experimental section) to obtain synthetically useful quantities. The adduct (**27**) takes the norcaradiene structure probably with a *syn* methylene–oxygen atom configuration ($\delta_H$ 0.36 and 2.81, *J* 4.7 Hz; $\delta_C$ 15.8, $J_{CH}$ 163 and 170 Hz). In contrast to the adduct with diphenyldithioliumolate, (**15a**), the MS of this adduct (**27**) showed an intense molecular-ion peak (62%), and the peak corresponding to the methano-oxonine (**28**) was relatively weak (20%). The adduct (**27**) is thermally stable, and it was recovered almost unchanged after being kept at 300 °C for 5 min. Attempted removal of the bridging oxygen atom from adduct (**27**) by treatment with tributylphosphine was unsuccessful. Irradiation (high-pressure mercury lamp) of a benzene solution of the adduct (**27**) gave a complex mixture of products. Chromatographic separation of the products gave low yields of fractions which were thought to consist mainly of the cyclohepta[*c*]furan (**17**; S = O) [*m/z* 284 (100%, *M*); $\delta_H$ 3.37, d, *J* 5.4 Hz] and the cyclohepta[*c*]pyridones (**20**; S = NPh) ($\nu_{max}$

* Europium tris-(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dionate).



**Scheme 2.** *Reagents and conditions:* i, heat; ii, *hν*; iii, MCPBA; iv, $Bu_3P$.



**Scheme 3.**

1 660 $cm^{-1}$; $\delta_H$ 2.81, d, *J* 6.1 Hz, and 2.88, d, *J* 6.3 Hz). However, no fraction suggestive of the presence of either the methano-oxonine (**28**) or the methano-oxecinone (**19**; S = NPh) could be found.

In a search for a better extrudable group, the reactions with the mesoionic 1,3-oxathiolium-4-olates (**29a** and **b**)[19] were tried. Although traces of the cycloadducts (**30**; R = Ph: $\delta_H$ 0.26 and 2.32, each d, *J* 5.0 Hz; $\delta_C$ 11.9, and (**30**; R = $COCF_3$: $\delta_H$ 0.32 and 2.22, each d, *J* 5.7 Hz) appeared to have been formed, they could not be isolated pure, and these reactions were not investigated further.

Complex product mixtures were formed on attempted preparation of the methanoazonines (**31**; R = Ph or H) by reaction with the mesoionic 3-methyl-2,4-diphenyloxazolium-5-olate (**32**)[20] or 3-methyl-2-phenylthiazolium-5-olate (**33**).[21] Mesoionic 1,2,3-triazolium-4-olates (**34a** and **b**),[22] a 1,2,3-triazolium-4-thiolate (**35**),[23] 3-phenylsydnone (**36**),[24] and a six-membered mesomeric 6-oxopyrimidinium-4-olate (**38**)[25] did not react at all with benzocyclopropene. If successful, these reactions would have given methanodiazonines (**37**) and a methanoazecinone (**39**).

From the results described above, we may conclude that the following two contradicting requirements should be satisfied for the successful preparation of methanoheteronines by this route:

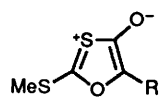
(1) Only a *stable and highly reactive* mesoionic compound can react with benzocyclopropene.

(2) The leaving group should be readily extrudable from the cycloadduct under relatively mild conditions. At the same time, the cycloadduct should preferably be stable enough to be isolated to avoid secondary reactions of the methanoheteronine in the reaction mixture.

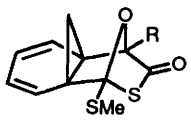
Reaction conditions such as cycloaddition under high pressure and flash pyrolysis may partially overcome the above restrictions.

As another drawback of this preparative route, unsubstituted methanoheteronines cannot be expected to be prepared because unsubstituted mesoionic compounds are rare.

*Reactions.*—The methanothiecinone (**19**) is thermally stable,



(29a) R = Ph
(29b) R = $CF_3CO$



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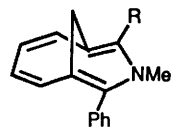

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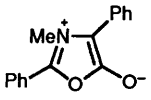

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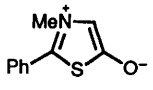

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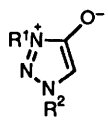
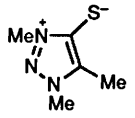


(34a) $R^1$ = $PhCH_2$, $R^2$ = Me
(34b) $R^1$ = Me, $R^2$ = $PhCH_2$



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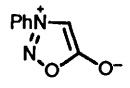

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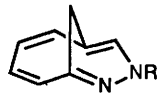

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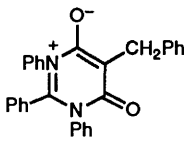

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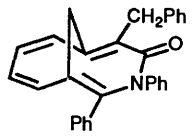


(39)

but the methanothionine (**16**) underwent clean isomerisation, on heating, to the cycloheptathiophene (**17**) probably by consecutive [1,5]-sigmatropic and electrocyclic reactions. This rearrangement did not occur by irradiation. This shows that methanothionine (**16**) is not an intermediate in the formation of the cycloheptathiophene (**17**) by photolysis of the cycloadduct (**15a**). The methanothionine (**16**) did not react with DMAD or *N*-phenylmaleimide, at least not at a rate faster than that at which it decomposed or isomerised. No reaction occurred between the methanothiecinone (**19**) and DMAD. The sluggish reactivity of these systems toward dienophiles is probably due to steric hindrance exerted by the phenyl and methylene groups. The methanothionine (**16**) did not react with morpholine, and complex reaction products were formed on treatment with hydrochloric acid or molecular oxygen, irradiation in the presence of oxygen, or dye-sensitised photo-oxidation. In many of these reactions, small amounts of the cycloheptathiophene (**17**) were formed among the reaction products (TLC, NMR).

*Aromaticity*.—The IR carbonyl band of the thiecinone (**19**) (1 635 $cm^{-1}$) appears at a higher frequency than that of the thiopyranone (**20**) (1 595 $cm^{-1}$). This shows that the polarisation of the carbonyl group of the thiecinone (**19**) is not very pronounced. The $^{13}C$–$^{1}H$ coupling constants (136–146 Hz) of the methylene bridges of the bridged heteroannulenes (**13**), (**16**), and (**19**) suggest that the C–C–C bond angles of these bridged carbons are larger than normal due to the conjugated annulene rings. Both the $^{1}H$ and $^{13}C$ NMR chemical shifts of the methylene bridges of the heteroannulenes (**13**), (**16**), and (**19**) are shifted downfield from those of the methano[10]annulene (**40**).[26] The proton NMR shifts of the diene portion are shifted upfield from those of methano[10]annulene (**40**) and the *o*-quinonoid benzo[*c*]heterocycles (**41**)–(**44**).[27] Although the chemical shifts of the monocyclic heteronines have not been completely analysed, they generally appear at even higher magnetic fields.[9] These spectroscopic data show that the degree of electronic delocalisation is not large in the bridged heteroannulenes and, accordingly, the diene portions are not highly deshielded and the degree of shielding of the bridged methylene group is small. However, a decisive conclusion cannot be reached until the effects exerted by the heteroatoms and the phenyl substituents can be correctly analysed. Phenyl substituents do not appear to exert a large effect on the chemical shifts of the *peri*-position protons [$\Delta\delta$ 0.07 ppm for *N*-methylisoindole (**43**) and its 1,3-diphenyl derivative (**44**)].[27]

The ratio of the coupling constants of the proton pairs on adjacent atoms of the diene portion of these bridged heteroannulenes fall within the range 0.71–0.77 (see Table). These values roughly correspond with the values of isobenzofuran (**41**) (0.70), isobenzothiophene (**42**) (0.72), isoindoles (**43**) and (**44**) (0.74), and thiophene (0.71). If the ratio of these *J*-values may be taken as a good criterion of bond alternation,[28] then it may be concluded that the degree of electronic delocalisation of the bridged heteroannulenes discussed above is almost the same as those of benzo[*c*]-furan, -thiophene, and -pyrrole, which are generally regarded as examples of typical *o*-quinonoid compounds. This conclusion appears to be in fair agreement with the theoretical work of Trinajstic and co-workers,[29] who predicted that the bridged heteronines should have smaller topological resonance energies than benzo[*c*]-furan, -thiophene, and -pyrrole, though larger than the corresponding monocyclic heteronines.

## Experimental

M.p.s were determined on a Yanagimoto hot-stage apparatus and are uncorrected. IR spectra (KBr) were recorded with a Hitachi 345 spectrophotometer. Unless otherwise stated, $^{1}H$ (90 MHz) and $^{13}C$ (22.5 MHz) NMR spectra were recorded with a JEOL JNM-FX-90Q spectrometer on solutions in deuteriochloroform (tetramethylsilane internal standard). Mass spectra were measured with a JEOL JMS-01SG-2 spectrometer. Merck Kieselgel 60 or Merck Kieselgel 60 $PF_{254}$ was used for chromatography. Irradiations were performed with a 100-W high-pressure mercury lamp through a Pyrex filter for solutions under argon below 20 °C with external cooling. Deaerated solvents were used throughout when the thionine (**16**) was involved. Yields are based on isolated products with sufficient purity.

9-*Phenyl*-8-*thia*-7-*azabicyclo*[4.3.1]*deca*-2,4,6,9-*tetraene* (**13**).—A solution of benzocyclopropene[30] (270 mg, 3.0 mmol) and the mesoionic oxathiazoliumolate (**12**) (537 mg, 3.0 mmol) in benzene (30 ml) was kept for 4 weeks in the dark under nitrogen at room temperature. Separations on column chromatography (dichloromethane–cyclohexane) and preparative TLC afforded a fraction which, on cooling, solidified to a yellow mass but which was still contaminated by small amounts of impurities. It darkened fairly rapidly, and it was not possible to isolate an analytically pure sample; $\lambda_{max}$(hexane) 258, 347, and 382 nm; $\delta_H(CH_2)$ 0.72 (1 H, dt, *J* 8.3 and 1.2 Hz) and 2.74 (1 H, d, *J* 8.3 Hz); $\delta_C(CH_2)$ 48.4 (ddt, *J* 146, 141, and 5 Hz); for additional NMR data, see Table and ref. 2*a*; *m*/*z* 225 ($M^+$, 68%), 224 ($M^+$ − H, 100), and 121 ($PhCS^+$, 29).

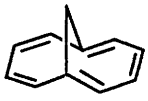
1,4-*Diphenyl*-1,4-*epithio*-4a,8a-*methano*-1H-2-*benzothiopyran*-3(4H)-*one* (**15a**).—A solution of the mesoionic dithioliumolate (**14**) (**13.5** g, 50 mmol) and benzocyclopropene (4.5 g, 50 mmol) in benzene was kept for 38 days in the dark under nitrogen at room temperature. Concentration of the solvent and recrystallisation from acetone afforded the *cycloadduct* (**15a**) as faintly pink prisms (7.4 g, 41%), m.p. 166–167 °C (Found: C, 73.5; H, 4.5; S, 17.6. $C_{22}H_{16}OS_2$ requires C, 73.3; H, 4.5; S, 17.8%); $\lambda_{max}$(hexane) 265 nm (log ε 3.28); $\nu_{max}$ 1 705 (C=O) and

**Table.** Chemical shifts and coupling constants of bridged annulenes.*

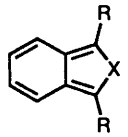
| Compound | A | B | C | D | |
|---|---|---|---|---|---|
| Thionine (**16**) | 7.09 | 6.11 | 6.11 | 7.09 | |
| Thiazonine (**13**) | 6.92 | 6.14 | 6.37 | 6.84 | |
| Thiecinone (**19**) | 7.14 | 6.33 | 6.39 | 6.87 | |

| | *J*(AB) | *J*(AC) | *J*(AD) | *J*(BC) | *J*(BD) | *J*(CD) | *J*(BC)/*J*(AB); *J*(BC)/*J*(CD) |
|---|---|---|---|---|---|---|---|
| (**16**) | $10.7_6$ | $0.0_5$ | $1.5_2$ | $7.9_7$ | $0.0_5$ | $10.7_6$ | 0.74 |
| (**13**) | $10.5_2$ | 0 | $1.5_0$ | $8.0_5$ | 0 | $10.8_2$ | 0.76; 0.74 |
| (**19**) | $11.0_0$ | $0.2_8$ | $1.4_5$ | $8.1_4$ | $0.2_6$ | $11.4_3$ | 0.74; 0.71 |

* The values in the Table were obtained by simulation. The calculated values of the thionine and thiecinone agreed within 0.17 Hz with the observed values. The deviation with the thiazonine is within 0.3 Hz. The thionine and the thiecinone were measured with a JEOL GX270 spectrometer (269.60 MHz) for 4 000 Hz by 131 072 sampling points, and the thiazonine was measured with a JEOL JNM-FX90Q spectrometer (89.6 MHz) for 896 Hz with 16K sampling points.



(**40**)



(**41**) X = O, R = H
(**42**) X = S, R = H
(**43**) X = NMe, R = H
(**44**) X = NMe, R = Ph

1 600 $cm^{-1}$; $\delta_H$ 0.56 (1 H, d, *J* 5.3 Hz, *H*CH *anti* to S), 3.58 (1 H, d, *J* 5.3 Hz, HC*H syn* to S), 5.9–6.2 (4 H, m, 5-, 6-, 7-, and 8-H), 7.2–7.5 (6 H, m, Ph), and 7.6–7.8 (4 H, m, Ph); $\delta_C$ 14.3 (dd *J* 169 and 163 Hz, $CH_2$), 34.1 (s, C-4a), 42.9 (s, C-8a), 78.0 (s, C-4), 79.5 (s, C-1), and 204.9 (s, C=O); *m*/*z* (20 eV) 360 ($M^+$, 1.4%), 300 ($M^+$ − SCO, 100), and 121 ($PhCS^+$, 53).

7,9-*Diphenyl*-8-*thiabicyclo*[4.3.1]*deca*-2,4,6,9-*tetraene* (**16**).—A solution of the adduct (**15a**) (720 mg) in xylene (60 ml) was heated under reflux for 1.5 h. Chromatographic separation ($CCl_4$) and recrystallisation at −50 °C (hexane) gave *compound* (**16**) as orange needles (373 mg, 62%), m.p. 121–122 °C (Found: C, 83.7; H, 5.2; S, 10.8. $C_{21}H_{16}S$ requires 84.0; H, 5.4; S, 10.7%); $\lambda_{max}$(hexane) 305 (4.16) and 410 nm (4.01); $\delta_H(CH_2)$ 1.15 (1 H, dt, *J* 4.0 and 1.2 Hz) and 2.29 (1 H, d, *J* 4.0 Hz); $\delta_C(CH_2)$ 46.0 (ddt, *J* 141, 137, and 5 Hz); for additional NMR data, see Table and ref. 2*a*; *m*/*z* 300 ($M^+$, 100%), 223 ($M^+$ − Ph, 66), 191 ($M^+$ − Ph − S, 30), and 121 ($PhCS^+$, 15).

1,3-*Diphenyl*-4H-*cyclohepta*[c]*thiophene* (**17**).—A solution of the adduct (**15a**) (500 mg) in benzene (350 ml) was irradiated for 28 h. Products from three such irradiations were combined and chromatographed (benzene–cyclohexane) to give *compound* (**17**) (276 mg, 22%) as lemon yellow prisms, m.p. 107–108 °C (Found: C, 83.8; H, 5.25; S, 10.7. $C_{21}H_{16}S$ requires C, 84.0; H, 5.4; S, 10.7%); $\delta_H$ 3.22 (2 H, d, *J* 5.9 Hz, 4-$H_2$), 5.30–6.30 (3 H, m, 5-, 6-, and 7-H), 6.85 (1 H, d, *J* 11.4 Hz, 8-H), and 7.1–7.5 (10 H, m, Ph); $\delta_C$ 28.0 (t, *J* 120 Hz, $CH_2$); *m*/*z* 300 ($M^+$, 100%), 223 ($M^+$ − Ph, 14), and 121 ($PhCS^+$, 15).

1,4-*Diphenyl*-1,4-*epithio*-4a,8a-*methano*-1H-2-*benzothiopyran*-3(4H)-*one* 10-*Oxide* (**18**).—A solution of the adduct (**15a**) (2.89 g, 8 mmol) and MCPBA (85% purity; 1.62 g, 8 mmol) in dichloromethane (70 ml) was kept for 7 h at room temperature. The solution was washed with aq. sodium hydroxide, then concentrated, and the residue was recrystallised from benzene–hexane to give the *sulphoxide* (**18**) (2.89 g, 96%), m.p. 225–226 °C (Found: C, 70.4; H, 4.1; S, 17.2. $C_{22}H_{16}O_2S_2$ requires C, 70.2; H, 4.3; S, 17.0%); $\lambda_{max}$ 247 nm (3.80); $\nu_{max}$ 1 715 (C=O), 1 495, 1 450, and 1 150 $cm^{-1}$; $\delta_H$ 0.90 and 3.19 (each 1 H, d, *J* 7.2 Hz, $CH_2$), 5.97–6.07 (2 H, m, 6- and 7-H), 6.08–6.45 (2 H, m, 5- and 8-H), and 7.26–7.83 (10 H, m, Ph); $\delta_C$ 14.26 (t, *J* 166 Hz, $CH_2$), 33.3 (s, C-4a), 38.4 (s, C-8a), 83.1 (s, C-4), 88.7 (s, C-1), and 199.1 (s, C=O); *m*/*z* 376 ($M^+$, trace), 328 ($M^+$ − SO, 100), 300, ($M^+$ − SO − CO, 21), and 121 ($PhCS^+$, 43).

2,5-*Diphenyl*-3-*thiabicyclo*[4.4.1]*undeca*-1,5,7,9-*tetraen*-4-*one* (**19**).—A solution of the adduct (**15a**) (1 g, 2.8 mmol) and tributylphosphine (756 mg, 3.7 mmol) in chloroform (8 ml) was refluxed for 10 h. The solution was concentrated and the residue was washed with cyclohexane to give practically pure *methanothiecinone* (**19**) (800 mg, 88%) as red prisms (from cyclohexane), m.p. 179 °C (Found: C, 80.3; H, 4.8; S, 9.7. $C_{22}H_{16}OS$ requires C, 80.5; H, 4.9; S, 9.8%); $\lambda_{max}$(MeCN) 254 (4.16), 288 (4.21), and 415 nm (2.81); $\nu_{max}$ 1 645 $cm^{-1}$ (C=O); $\delta_H$ ($CH_2$) 2.14 (1 H, d, *J* 11.2 Hz) and 2.58 (1 H, dt, *J* 11.2 and 1.6 Hz); see also Table; $\delta_C$ 37.5 (dd, *J* 136 and 138 Hz, $CH_2$) and 190.5 (s, C=O); *m*/*z* 328 ($M^+$, 100%), 300 ($M^+$ − CO, 20), 299 ($M^+$ − CO − H, 24), and 121 ($PhCS^+$, 34).

*Photolysis of the Sulphoxide* (**18**).—A solution of the sulphoxide (**18**) (300 mg) in benzene (250 ml) was irradiated for 41 h. The products were separated by chromatography (dichloromethane) to give the thiecinone (**19**) (38 mg, 15%) and a mixture of 1,4-*diphenylcyclohepta*[c]*thiopyran*-3(5 H and 9 H)-*one* (**20a**) and (**20b**) (ratio 1:2.6) (115 mg, 44%), m.p. 189–190 °C (Found: C, 80.7; H, 4.9; S, 9.6. $C_{22}H_{16}OS$ requires C, 80.5; H, 4.9; S, 9.8%); $\nu_{max}$ 1 595 $cm^{-1}$ (C=O); $\delta_H$ 2.91 and 2.96 (total 2 H, d, *J* 6.1 Hz, $CH_2$), 5.97–6.80 (4 H, m, =CH), and 7.10–7.50 (10 H, m, Ph); $\delta_C$ 31.8 and 35.1 (t, *J* 130 and 135 Hz, $CH_2$), and 183.8 and 184.7 (s, C=O); *m*/*z* 328 ($M^+$, 13%) and 300 ($M^+$ − CO, 47).

*Thermal Isomerisation of the Methanothionine* (**16**).—A toluene solution (3 ml) of the methanothionine (**16**) (20 mg) was heated under reflux for 7.5 h. Concentration, and washing with a small amount of hexane, gave the cycloheptathiophene (**17**) (17 mg, 85%), identical with an authentic specimen.

4-*Methyl*-1-*phenyl*-1,4-*epithio*-4a,8a-*methano*-1H-2-*benzothiopyran*-3(4 H)-*one* (**22**).—A mixture of the dithioliumolate (**21**) (15.7 g) and benzocyclopropene (6.82 g) in benzene (500 ml) was stirred at 50 °C for 4 days under argon with exclusion of moisture. The mixture was filtered, the filtrate was concentrated, and the residue was extracted with hexane. The hexane extract was recrystallised from hexane–diethyl ether to give the *adduct*

(**22**) (3.57 g, 17%), m.p. 125 °C (Found: C, 68.2; H, 4.8; S, 21.5. $C_{17}H_{14}OS_2$ requires C, 68.4; H, 4.7, S, 21.5%); $\nu_{max}$ 1 704 $cm^{-1}$; $\delta_H$ 0.27 and 3.24 (each 1 H, d, *J* 5.5 Hz, $CH_2$), 1.80 (3 H, s, Me), 5.90–6.23 (4 H, m, 5-, 6-, 7-, and 8-H), 7.37–7.52 (3 H, m, Ph), and 7.62–7.80 (2 H, m, Ph); $\delta_C$ 11.7 (q, Me), 13.1 (dd *J* 164 and 168 Hz, $CH_2$), 35.3 (s, C-4a), 42.3 (s, C-8a), 73.1 (s, C-4), 79.0 (s, C-1), and 205.9 (s, C=O); *m/z* 298 ($M^+$, 63%), 270 ($M^+$ − CO, 21), 266 ($M^+$ − S, 5) 238 ($M^+$ − SCO, 100), 237 ($M^+$ − SCO − H, 64), 223 ($M^+$ − SCO − Me, 43), 161 ($M^+$ − SCO − Ph, 20), and 121 ($PhCS^+$, 31).

2,3,5-*Triphenyloxazolium*-4-*olate* (**26**).—This was prepared by a modification of Haddadin's procedure:[18] Phenylglyoxylanilide was prepared (57%) by oxidation of mandelanilide with dicyclohexylcarbodi-imide and dimethyl sulphoxide and the anilide was then converted into the *N*-benzoyl derivative (76%) by successive treatment with sodium hydride and benzoyl chloride. The oxazolium-4-olate (**26**) was prepared (46%) by refluxing a solution of the *N*-benzoyl derivative (5 g) and triethyl phosphite (15 ml) in toluene (40 ml) under argon.

1,2,4-*Triphenyl*-1,2-*dihydro*-1,4-*epoxy*-4a,8a-*methanoisoquinolin*-3(4H)-*one* (**27**).—A solution of the oxazoliumolate (**26**) (2.22 g) and benzocyclopropene (0.75 g) in deaerated anhydrous benzene (150 ml) was stirred for a week at 35 °C under argon with exclusion of moisture. Chromatography (dichloromethane) gave the *adduct* (**27**) (1.17 g, 41%) as needles, m.p. 156–157 °C (from acetone) (Found: C, 83.5; H, 5.1; N, 3.4. $C_{28}H_{21}NO_2$ requires C, 83.35; H, 5.25; N, 3.5%); $\lambda_{max}$(MeCN) 242 nm (4.06); $\nu_{max}$ 1 725 $cm^{-1}$ (C=O); $\delta_H$ 0.36 and 2.81 (each 1 H, d, *J* 4.7 Hz, $CH_2$), 5.90–6.05 (2 H, m, 6- and 7-H), 6.18–6.48 (2 H, m, 5- and 8-H), and 6.8–8.0 (10 H, m, Ph); $\delta_C$ 15.8 (dd, *J* 163 and 170 Hz, $CH_2$), 34.9 (s, C-4a), 40.3 (s, C-8a), 86.6 (s, C-4), 99.7 (s, C-1), and 172.7 (s, C=O); *m/z* 403 ($M^+$, 62%), 375 ($M^+$ − CO, 94), 284 ($M^+$ − PhNCO, 20), 178 ($M^+$ − PhNCO − PhCO − H, 94), 119 (PhNCO, 100), and 105 ($PhCO^+$, 100).

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