Aromaticity in Bridged Heteroannulenes

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The aromatic stabilities of bridged hetero[n]annulenes (n = even, odd) and the parent structures of hetero-[n]annulenes and hetero[n]polycycles have been predicted by the topological resonance energy, TRE, approach. The TRE criterion places bridged structures in all cases studied between the hetero[n]annulenes and hetero[n]polycyclic systems. The extra aromatic stability of the bridged heteroannulenes compared to heteroannulenes is attributed to homoaromatic interaction across the ring at the bridge sites. Available experimental evidence supports the theoretical results.

Introduction.

Experimental and theoretical work on [n]annulenes and bridged [n]annulenes is abundantly documented [2-26]. Recent years have witnessed an increasing of synthetic work on hetero[n]annulenes [27-33]. Much less work has been carried out on the bridged hetero[n]annulenes, especially on those with n = odd [9,10,34-39]. This fact is really surprising, because the work on the annulenes and bridged annulenes has shown that the bridged [n]annulenes possess greater aromatic stability than the corresponding [n]-annulenes, and that their preparation is only a matter of an appropriate synthetic technique [10]. Since many analogies between the annulene and heteroannulene chemistry hold [6,9,10,30], one may expect that the above will also be valid for hetero[n]annulenes and bridged hetero[n]annulenes. This question will certainly be settled in time to come by accumulating experimental evidence. In the meantime, we decided to study aromaticity in hetero[n]an-

nulenes and the corresponding bridged hetero[n]annulenes by means of a theoretical model called the topological resonance energy [40-42] with hope that our predictions will be used as helpful guidance for the chemists interested in making the bridged hetero[n]annulenes.

Here we are concerned with a class of the bridged hetero[n]annulenes, containing a single heteroatom which may be formally constructed from hetero[n]annulenes by inserting the bridge between the appropriate sites on the heteroannulene ring. The bridge is ordinarily the -CH_2- group [8]. Heteroannulenes with a single heteroatom may be partitioned into two groups depending on whether n is even or odd. Hetero[n]annulenes with n = even may formally be generated from [n]annulenes by replacing one carbon atom with a heteroatom bearing a single π electron, *e.g.*, the imine nitrogen. Hetero[n]annulenes with n = odd may formally be generated from [n]annulenes by replacing the -CH=CH- group with a heteroatom bearing two π elec-
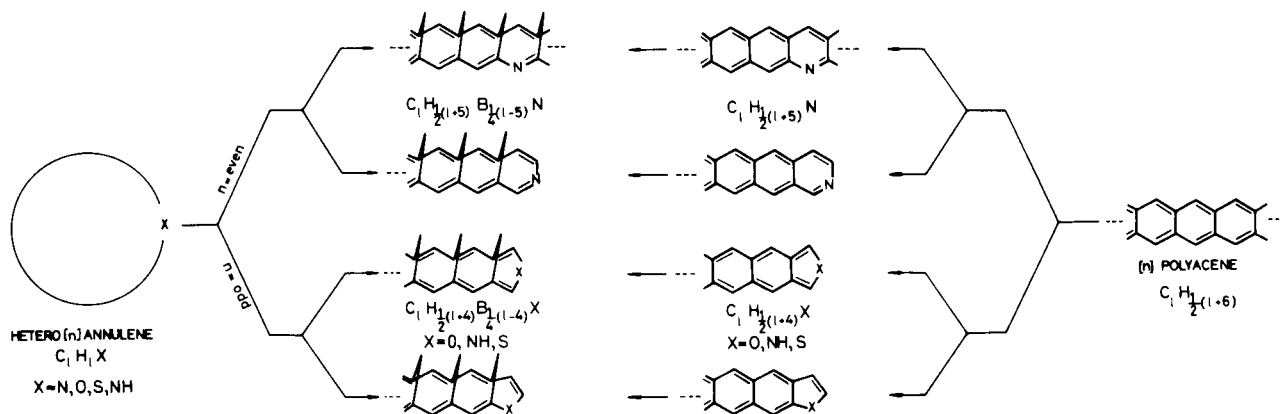

Figure 1. Schematic construction of the bridged hetero[n]annulenes. B symbolizes the bridge fragment.

trons, *e.g.*, the ether oxygen, the amine nitrogen, or the divalent sulfur. Alternatively, the bridged hetero[n]annulenes may also formally be derived from either aza-polyacenes or polycyclic structures obtained by a linear annelation of acenes and furan, pyrrole, or thiophene by insertion of an atom or a group into the bonds common to two rings and thus produce the bridge. Aza-polyacenes may formally be obtained from polyacenes by exchanging one carbon atom for the imine nitrogen, while linear polycyclic structures containing a five-membered heterocycle: furan, pyrrole, or thiophene, are generated from polyacenes by replacing a -HC=CH- fragment with ether oxygen or the amine nitrogen or the divalent sulfur, respectively. The above is illustrated in Figure 1. The atom or the group making the bridge is symbolized by B.

We assume that the bridged hetero[n]annulene is a delocalized structure in which there is a considerable homoaromatic interaction across the molecule at the bridge ends. Here we have merely transplanted the homoaromatic model used for bridged annulenes [22,24,43] to bridged hetero[n]annulenes. In the case of bridged [n]annulenes, it is accepted by most chemists [44] that the bridge sites of the annulene system in the bridged structure are linked by the through-space homoconjugative interactions [45-57]. The magnitude of the transannular interaction is a crucial quantity for the homoaromatic model of bridged annulenes. It has been estimated by Dewey *et al.* [56] that the transannular interaction is about 40% of that between the adjacent $2p_z$ orbitals in benzene. This value was adopted in our work [22] and in the work by Herndon and Párkányi [24] on the bridged [n]annulenes and it is used in the present paper.

Theory.

In the present work we investigated the aromatic stability of bridged hetero[n]annulenes in the same way as we studied the stability of [n]annulenes [20] and bridged [n]-annulenes [22] using the topological resonance energy (TRE) model [40-42,58,59]. The TRE model has been shown, in spite of some limitations [60-62], to be a useful model for predicting aromaticity in various classes of conjugated systems [22,41,42,58,59,62-70].

We are quite aware that aromaticity is a very controversial concept [71,72]. However, it is so deeply present in everyday chemical thinking that neither is it likely to be replaced by an ersatz concept nor is it likely to be rejected [73-80]. The use of the term *aromatic*, since its inception, was never quantitative, though various aromaticity indices, such as the one we use, may serve as a quantitative criterion for the comparison of different conjugated structures [81]. We use the TRE index as a device for classifying conjugated structures into three very broad groups: aromatic, non-aromatic, and anti-aromatic species. This

classification should serve as an indicator for experimental chemists who know from their experience that a molecule labeled aromatic is usually easier to make than one labeled anti-aromatic [73,77,78]. Therefore, in this work we wish to classify the bridged hetero[n]annulenes according to their aromatic characters and compare them with the parent structures: hetero[n]annulenes and hetero[n]polycycles by using the TRE index.

The numerical values of the TRE indices can be obtained from the following formula [22],

$$TRE = \sum_{j=1}^{N} g_j(x_j - x_j^{ac}) \qquad (1)$$

where x_j's are the Hückel eigenvalues, while x_j^{ac}'s are those of the acyclic (reference, matching) polynomial [69,82]. The g_j is the orbital occupancy number. The acyclic polynomial is used in the TRE model to represent the   Dewar-type acyclic reference structure [76]. The computation of the TRE and the computer program is detailed elsewhere [83]. The TRE index may be interpreted as the degree of aromatic stabilization of a cyclic conjugated system in the ground state. It represents the difference between the total π electron energy of a conjugated molecule and the total π electron energy that the conjugated molecule would possess if it were olefinic in nature.

In order to avoid the size effect, the TRE is normalized [84],

$$TRE(PE) = \frac{TRE}{N} \qquad (2)$$

where TRE(PE) stands for TRE per π electron, while N is the number of π electrons in the conjugated molecule. The threshold values of TRE(PE) used for classifying conjugated systems are as follows: (i) molecules having TRE(PE) equal or larger than 0.01 are considered to be of prevailing aromatic character; (ii) molecules having TRE(PE) values in the interval $+0.01$, -0.01 are either ambivalent or non-aromatic species, and (iii) molecules having TRE(PE) equal or smaller than -0.01 are viewed as anti-aromatic.

We also give for each molecule studied the percentage of its benzene character, which is calculated by means of the formula,

$$\% = \frac{TRE(PE)(molecule)}{TRE(PE)(benzene)} \cdot 100 \qquad (3)$$

where TRE(PE) (benzene) = 0.046 (42). This is done because some people [6] think that the only truly aromatic compound is benzene. Therefore, benzene is selected as

the representative aromatic compound. The above is a measure that determines how close to or far from benzene stability a given compound is. In addition, it may be used for differentiating molecules within a given class of compounds if they all are, for example, labeled aromatic by the criterion described above.

The π systems of the bridged hetero[n]annulenes are depicted by the appropriate vertex- and edge-weighted molecular graphs (85) G_{VEW}. The homoaromatic interaction across the annulene ring is denoted in G_{VEW} by the edge (bond) with "weight" k [22,24,67]. An example of the vertex- and edge-weighted graph representing bridged hetero[9]annulenes is given in Figure 2.
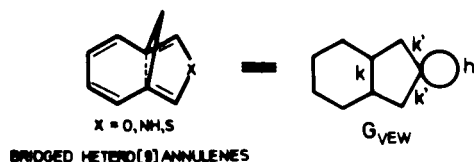

Figure 2. Example of the vertex- and edge-weighted graph G_{VEW} of a bridged hetero[n]annulene.

The heteroatomic and heterobond parameters for X and C-X (X=N, O, NH, S) are taken from Hess and Schaad [86-88]. The value for the homoaromatic parameter k is taken to be 0.4. However, we carried out several sets of TRE calculations varying k from 0.00 (aza[10]annulene, thiepin) to 1.00 (quinoline, isothionaphthene) in steps of 0.10. Results are shown in Figure 3.
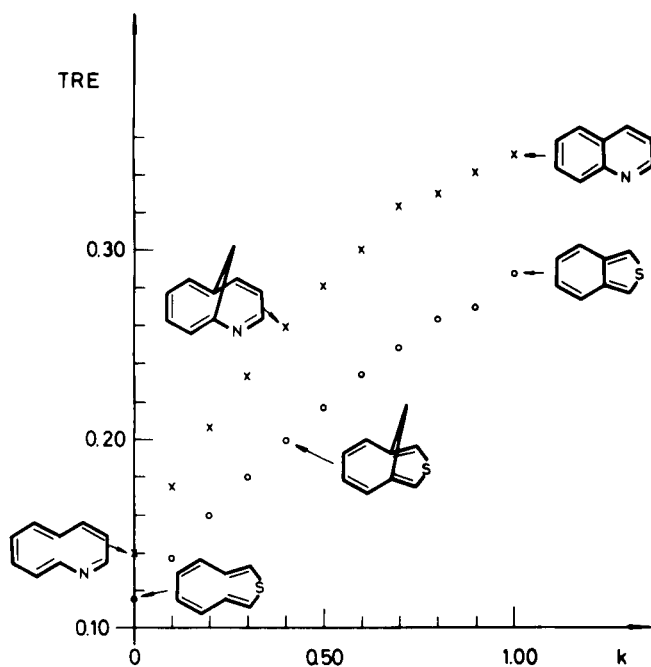
We see that the TRE variations are smooth from the no-bridge structures to the structures with the proper trans-annular bond.

The final point we wish to discuss in this section is the assumption that the annulene part of the bridged structure is planar and that the only effect in operation within the bridged molecule is the homoaromatic interaction. In this model we have oversimplified the real picture of the bridged structure. It appears that the perturbed annulene ring in the bridged molecule is not really planar [55]. The degree of non-coplanarity depends on the bridging group. However, the homoaromatic model of bridged (hetero)[n]-annulenes is in the first approximation quite adequate, and in the case of bridged [n]annulenes, as shown by Herndon and Párkányi [24], is supported by a good agreement between calculated and experimental properties of these molecules.

Results and Discussion.

The molecules studied in this work are divided into six families (see Figure 1). The schematic representation of each family is given in a different figure. Thus, aza[n]annulenes are given in Figure 4, odd-membered hetero[n]annulenes containing O, S, or NH in Figure 5, linear aza-benzenoids in Figure 6, benzo- and linear naphtho- and anthro-furans, anthro-pyrroles, and anthro-thiophenes in Figure 7, bridged aza[n]annulenes in Figure 8, and bridged odd-membered hetero[n]annulenes in Figure 9.
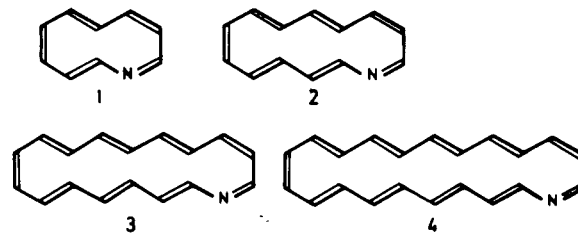

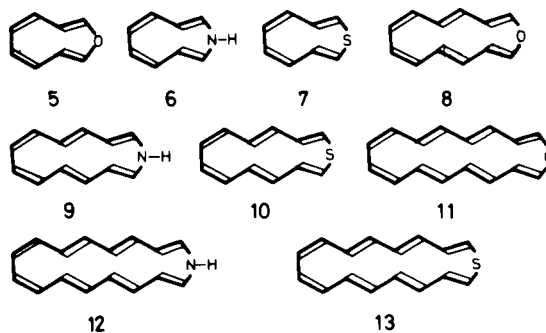Figure 4. Schematic representation of the aza[n]annulenes.

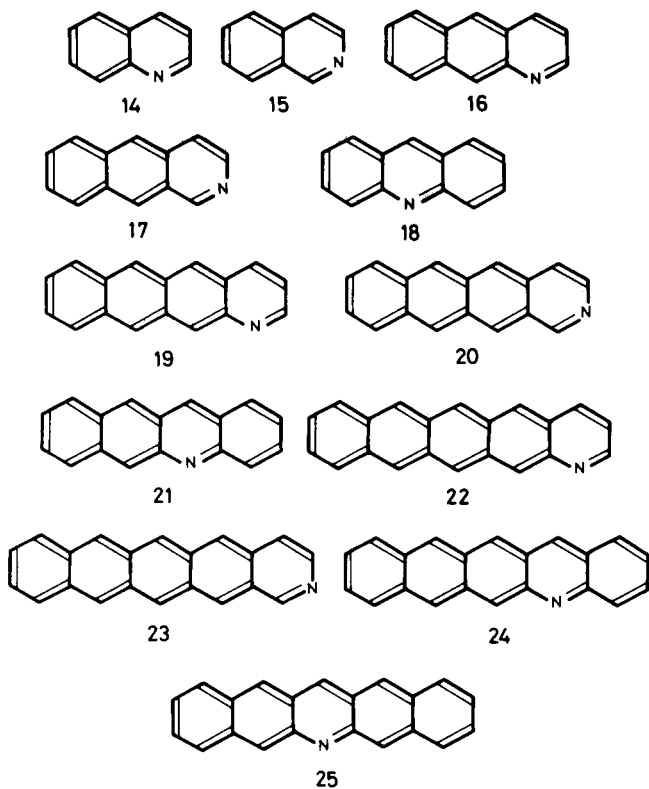Figure 5. Schematic representation of the odd-membered hetero[n]annulenes containing O, S, or NH.

Figure 3. TRE *vs.* homoconjugative parameter k for bridged aza[10]annulene and bridged thiepin.

Figure 6. Schematic representation of linear aza-benzenoids related to the aza[n]annulenes from Figure 4.
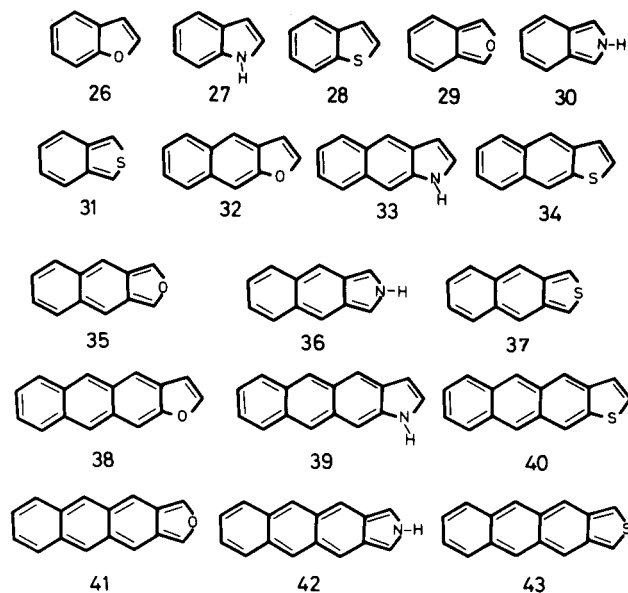

Figure 7. Schematic representation of benzo-, and linear naphtho- and anthro-furans, anthro-pyrroles, and anthro-thiophenes.
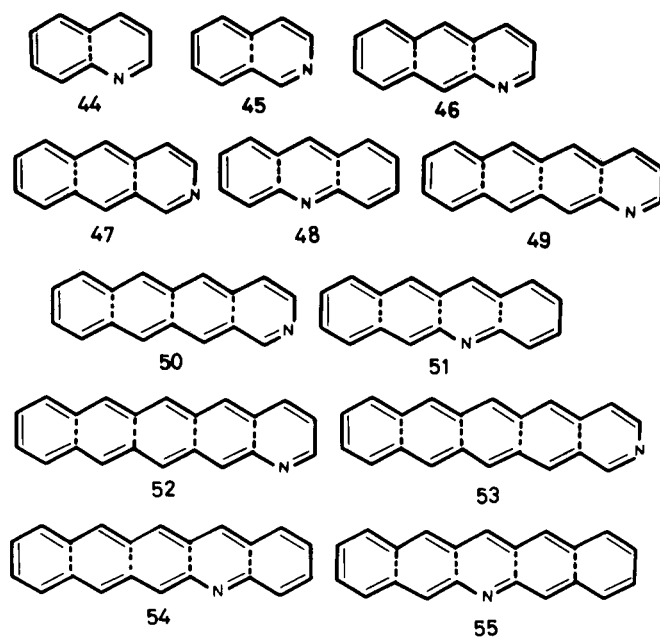
Figure 8. Schematic representation of the bridged aza-[n]annulenes derived from the aza[n]annulenes in Figure 4. The bridge is denoted by the broken line.
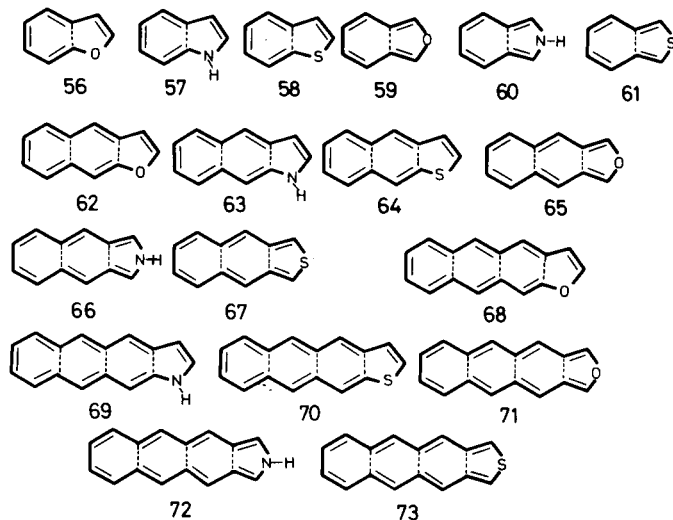
Figure 9. Schematic representation of the bridged odd-membered hetero[n]annulenes containing O, S, or NH. The bridge is denoted by the broken line.

The TRE, TRE(PE) values, the predicted status (A = aromatic, NA = non-aromatic), and the percentage of the benzene character for molecules 1-4 (Figure 4), 5-13 (Figure 5), 14-25 (Figure 6), 26-43 (Figure 7), 44-55 (Figure 8), and 56-73 (Figure 9) are given in Table 1, Table 2, Table 3, Table 4, Table 5, and Table 6, respectively.

Table 1

TRE and TRE(PE) Values of the Aza[n]annulenes

Aza[n]-annulene [a]	TRE	TRE(PE)	Predicted status	% of the benzene character	Reference to the preparative work
1	0.123	0.012	A	27	91
2	0.101	0.007	NA	16	83
3	0.079	0.004	NA	10	90
4	0.065	0.003	NA	7	

[a] Structures of the aza[n]annulenes studied are depicted in Figure 4.

Table 2

TRE and TRE(PE) Values of the Odd-membered Hetero[n]annulenes Containing O, S, or NH

Hetero[n]-annulene [a]	TRE	TRE(PE)	Predicted status	% of the benzene character	Reference to the preparative work
5	0.024	0.0002	NA	5	30
6	0.134	0.013	A	29	30
7	0.116	0.012	A	26	
8	0.017	0.001	NA	3	
9	0.093	0.007	NA	15	99
10	0.082	0.006	NA	13	
11	0.013	0.001	NA	2	100
12	0.071	0.004	NA	9	100
13	0.064	0.0036	NA	8	

[a] Structures of the odd-membered hetero[n]annulenes studied are depicted in Figure 5.

Table 3

TRE and TRE(PE) Values of Linear Aza-benzenoids

Aza-benzenoids [a]	TRE	TRE(PE)	Predicted status	% of the benzene character	Reference to the preparative work
14	0.350	0.036	A	78	102
15	0.351	0.035	A	77	103, 114
16	0.444	0.032	A	70	104
17	0.439	0.031	A	69	104
18	0.289	0.021	A	45	105
19	0.523	0.029	A	64	106
20	0.519	0.029	A	63	106
21	0.542	0.030	A	66	107
22	0.599	0.027	A	60	
23	0.596	0.027	A	60	
24	0.621	0.028	A	62	108
25	0.626	0.028	A	63	109

[a] Structures of the linear aza-benzenoids studied are depicted in Figure 6.

Table 4

TRE and TRE(PE) Values of Benzo-, and Linear Naphtho- and Anthro-derivatives of Furan, Pyrrole, and Thiophene

Hetero-polycyclic compounds [a]	TRE	TRE(PE)	Predicted status	% of the benzene character	Reference to the preparative work
26	0.272	0.027	A	60	119
27	0.375	0.038	A	83	120
28	0.349	0.035	A	77	121
29	0.114	0.011	A	25	122
30	0.323	0.032	A	71	123, 124
31	0.288	0.029	A	63	125
32	0.386	0.028	A	61	
33	0.462	0.033	A	73	
34	0.440	0.031	A	69	126
35	0.198	0.014	A	31	
36	0.398	0.028	A	63	127
37	0.367	0.026	A	58	128
38	0.472	0.026	A	58	
39	0.539	0.030	A	66	
40	0.519	0.029	A	63	129
41	0.283	0.016	A	35	
42	0.472	0.026	A	58	
43	0.444	0.025	A	54	130

[a] Structures of heteropolycyclic compounds consisting of benzo-, naphtho-, or anthro-part linearly attached to eithr furan, pyrrole, or thiophene are depicted in Figure 7.

Table 5

TRE and TRE(PE) Values of the Bridged Aza[n]annulenes

Bridged Aza[n]-annulene [a]	TRE	TRE(PE)	Predicted status	% of the benzene character	Reference to the preparative work
44	0.265	0.026	A	58	32, 36, 37,131
45	0.259	0.026	A	57	34, 132, 133
46	0.297	0.021	A	47	
47	0.291	0.021	A	46	
48	0.311	0.022	A	49	
49	0.328	0.018	A	40	
50	0.324	0.018	A	40	
51	0.345	0.019	A	42	
52	0.359	0.016	A	36	
53	0.355	0.016	A	36	
54	0.377	0.017	A	38	
55	0.380	0.017	A	38	

[a] Structures of the bridged aza[n]annulenes studied are depicted in Figure 8.

Aza[n]annulenes.

Aza[10]annulene (1) is predicted to be an aromatic structure, aza[14]annulene (2), marginally aromatic, while aza-[18]annulene (3), and aza[22]annulene (4) are predicted to be non-aromatic species. Experimental data [83,90] for 2

and **3** support this prediction. No reports are found in literature on the preparation of **1** and **4**. However, aza[10]-annulene is postulated as an intermediate monocycle in

Table 6

TRE and TRE(PE) Values of the Bridged Odd-membered Hetero[n]annulenes

Bridged odd-membered hetero[n]-annulenes [a]	TRE	TRE(PE)	Predicted status	% of the benzene character	Reference to the preparative work
56	0.184	0.018	A	40	
57	0.283	0.028	A	62	
58	0.262	0.026	A	58	
59	0.064	0.006	NA	14	
60	0.226	0.023	A	50	
61	0.199	0.020	A	44	38
62	0.247	0.018	A	39	
63	0.315	0.023	A	50	
64	0.300	0.021	A	47	
65	0.095	0.007	NA	15	
66	0.244	0.017	A	38	
67	0.221	0.016	A	35	
68	0.291	0.016	A	36	
69	0.346	0.019	A	42	
70	0.333	0.019	A	41	
71	0.127	0.007	NA	16	
72	0.248	0.015	A	33	
73	0.248	0.014	A	30	

[a] Structures of the bridged odd-membered hetero[n]annulenes containing O, S, or NH are depicted in Figure 9.

the preparation of azanaphthalenes [91]. Theoretical predictions for aza[n]annulenes are comparable to those for [n]annulenes [92,93]. [10]Annulene is predicted to be aromatic, while [14]-, [18]-, and [22]annulenes are predicted to be borderline aromatic compounds which with increase in the size are becoming more and more non-aromatic. All these [n]annulenes have been made [2,94-96] and their properties are in agreement with the above predictions.

Odd-membered Hetero[n]annulenes.

Hetero[9]annulenes are called heteronins [27]. We predict oxonin (**5**) to be non-aromatic, while azonine (**6**) and thionine [7] should be aromatic. Oxonin and azonine have been prepared [30]. These two compounds differ considerably in their stabilities and properties. On this basis oxonine is classified as a polyenic heterocycle, while azonine is an aromatic heterocycle in nice agreement with our predictions. Thionin has not yet been reported, although our prediction indicates that its aromatic stability should be comparable to that of azonine. Thionin has so far been reported only as a transient species [30]. Apparently in the case of heteronins two opposite effects operate. These are aromatic stability and skeletal strain. In the case of oxon-

in, both effects are most probably balanced, producing a polyenic heterocyclic structure. Azonine is presumably the case where the balance is on the side of aromatic stability and the molecule behaves as an aromatic species. Thionin, on the other hand, is probably the case where the balance is on the side of skeletal strain (due to much longer C-S bonds (1.73 Å) in comparison with C-N (1.43 Å) or C-O bonds (1.36 Å) [97]), which is relieved by distortion from coplanarity by valence tautomerism. In the case of thionin, a valence tautomer thus obtained probably gives sulfur away easily and the desired molecule is not obtainable. However, 4,5:6,7-dibenzothionin has been prepared, but the nmr and uv spectra indicate that this molecule is a non-aromatic species existing in buckled non-planar conformation [98]. This result supports the above idea of an unstable valence tautomer of thionin which is now stabilized by two benzene rings attached to the heteronin nucleus.

All three hetero[13]annulenes **8, 9,** and **10** are predicted to be non-aromatic. Only aza[13]annulene (**9**) has been reported [99], and its behaviour is that of the cyclopolyenic structure. Similarly, all three hetero[17]annulenes are predicted to be non-aromatic. Oxa[17]annulene and aza[17]annulene have been reported [100], and both show olefinic behaviour.

Aza-benzenoids.

All aza-benzenoids (N-arenes) are predicted aromatic since they all have rather high values of the TRE(PE) indices. This result is in accordance with other theoretical predictions [41,88,101], though these are usually limited to aza-naphthalenes and acridine. However, the predictions for lower aza-benzenoids (aza-naphthalenes and aza-anthracenes) are supported by the experimental findings [102-105]. For higher aza-benzenoids (aza-tetracenes, aza-pentacenes) the situation is not as clear-cut since the preparation of larger aza-benzenoids is rather difficult. Actually the synthetic efforts lead easily to diketo derivatives instead of the parent compounds [106-109]. Apparently in the case of large linear aza-benzenoids, as in the case of large linear polyacenes, the thermodynamic stability gradually diminishes with the increasing size while the reactivity (e.g., photo-oxidation) increases dramatically. This is also supported by theory: the variation in the percentage of the benzene character is between 78% (1-azanaphthalene) and 63% (6-azapentacene), while the HOMO-LUMO separation with the increasing size of the aza-benzenoids drops from 1.12 (56% of that in benzene) in 2-azanaphthalene to only 0.41 (22% of that in benzene) in 5-azapentacene. (These values are in β units).

Recent years have witnessed an increasing interest in aza-benzenoids, because they appear to be unique precursors [110-112] for the preparation of some rather complicated molecules such as aza-steroids. In addition they pos-

sess quite unusual biological properties which range from carcinogenecity to anti-cancer effects [111,113]. Efforts have been made to devise simpler synthetic schemes for some long known aza-benzenoids, such as the preparation of isoquinoline [114]. However, all this experimental work is directed to angular azabenzenoids which are much more stable than the corresponding linear isomers. For example, acridine (TRE = 0.289, TRE(PE) = 0.021) is predicted to be less stable than the phenanthridine (TRE = 0.511, TRE(PE) = 0.0326). This result is in fine agreement with experimental findings [115,116].

Heteropolycycles.

In this group we studied the benzo-, and linear naphtho- and anthro-derivatives of furan, pyrrole, and thiophene. All the systems studied are predicted to be aromatic. In all cases the furan derivatives always have the lowest TRE and TRE(PE) values and the lowest percentage of benzene character. This parallels the aromatic character of furan, pyrrole, and thiophene, which are predicted by various aromaticity indices to be as follows [40,41,86,87,117],

Furan ≪ Pyrrole > Thiophene
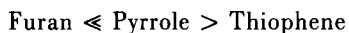
In addition, in all theoretical studies furan is found to be a non-aromatic species, while pyrrole and thiophene are aromatic. Experimental evidence supports this prediction [86,87]. Benzo-, naphtho-, or anthro-annelation stabilizes the furan nucleus and the whole system becomes aromatic.

In general, the annelation of benzene or naphthalene or anthracene and a conjugated 5-membered heterocycles containing a single heteroatom leads to bicyclic, tricyclic or tetracyclic molecules, isoelectronic with naphthalene, anthracene or tetracene, which fall distinctly into two classes depending on where the annelation occurs on the 5-membered rings. If the annelation happens at the short bond the resulting compounds belong to the "normal" class (26-28, 32-34, 38-40). In this class the arene moiety retains geometry close to the one in the parent structure. If annelation occurs at the long bond of the 5-membered ring the resulting compounds have the quinonoid structure in which the arene part has a distorted geometry. The latter always have a lower aromatic character than the "normal" isomers. These two classes also differ in other properties, besides the difference in the aromatic behavior and structure [118]. The experimental findings support the above reasoning [119-130].

Bridged Aza[n]annulenes.

The bridged aza[n]annulenes, studied in this work, are all predicted to be aromatic. However, the degree of aromaticity gradually drops with the increasing size of the aza-annulene part of the molecule. This prediction parallels that observed for bridged [n]annulenes [22,24].

We observe here another similarity with annulenes. In our earlier work it was noticed that the homoaromatic interaction across the annulene ring stabilizes the bridged structure. The similar relationship between the aza[n]annulenes and the corresponding bridged aza[n]annulenes is also found here.

The experimental work on bridged aza[n]annulenes has so far been limited to the first two members of the series [10,34,36,37,131-133]. In this case the experimental evidence and the theoretical prediction agree. Many more interesting experimental findings are expected in this area.

Bridged Odd-membered Hetero[n]annulenes.

All compounds in this class, except three bridged oxo-annulenes with the bridges symmetrically placed, are predicted to be aromatic. The three bridged oxo-annulenes: **59, 65,** and **71,** are predicted to be non-aromatic.

Bridged odd-membered hetero[n]annulenes form a little known class of bridged annulenes. Very limited experimental work on them has been carried out. We could find only one paper [38] reporting a preparation of the derivative of the structure **61** (bridged thionin). Methanothionin **61** does not undergo Diels-Alder cycloaddition with dimethyl acetylendicarboxylate or N-phenylmaleimide [39]. However, this probably should not be taken as evidence in support of its strong aromatic character, but rather as the result of steric hindrance by the flanking two phenyl groups and the methano-bridge. Our prediction that compound **61** is aromatic implies that the thionin part of methanothionin is planar. However, the ^{13}C-^{1}H coupling constant values [39] suggest that the thionin part of **61** is non-planar and considerably strained. Therefore, our TRE value probably overestimates the degree of aromatic character of the real molecule **61**. The electron delocalization in the real system should be smaller because of its deviation from coplanarity. Similarly, the degree of homo-conjugation along the bridgehead positions should also be smaller in the real system because of the longer C-S distances. Interestingly the parent structure, thionin, has not yet been reported. We predict both structures to be aromatic, but thionin is predicted weakly aromatic: compared to benzene aromaticity it is 50% less stable than the bridged thionin. This again confirms our earlier observation [22] that *the bridged annulene structure is always more stable than the parent annulene structure.* This additional stabilization comes from the homoaromatic interactions across the ring at the bridge sites.

We expect a lot of exciting experimental, and further theoretical, work on this class of bridged rings [134,135].

Concluding Remarks.

In this investigation we studied aromaticity in bridged heteroannulenes by means of a theoretical model called the topological resonance energy. Bridged heteroannul-

enes were then compared to the corresponding heteroan-nulenes and heteropolycycles. It appears that the bridged structures always show greater aromatic stability than the corresponding annulene. On the other hand, the bridged heteroannulenes are always predicted to possess a lower degree of aromatic stability than the corresponding hete-ropolycyclic structures. Therefore, the following stability order for these structures may be given:

(hetero)annulenes < bridged (hetero)annulenes
< (hetero)polycycles
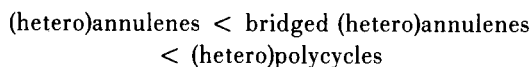
The additional stability of the bridged structure is attri-buted to the homoaromatic interaction across the ring. As this interaction becomes stronger the aromatic stability of the system increases. Finally, when a bond replaces the bridge a rather stable polycyclic system emerges. We should emphasize here that the norcaradienic forms of the bridged structures (see Figure 10) are not aromatic struc-tures, although it has been found [25] that the barrier separating, for example, the norcaradienic form from the annulenic isomer of 1,6-methano[10]annulene is very small. It is interesting to note that Kato [39] predicts that methano-bridged compounds of the type **56, 57, 58**, *etc.* would exist as their norcarardiene tautomers rather than the bridged annulenes.
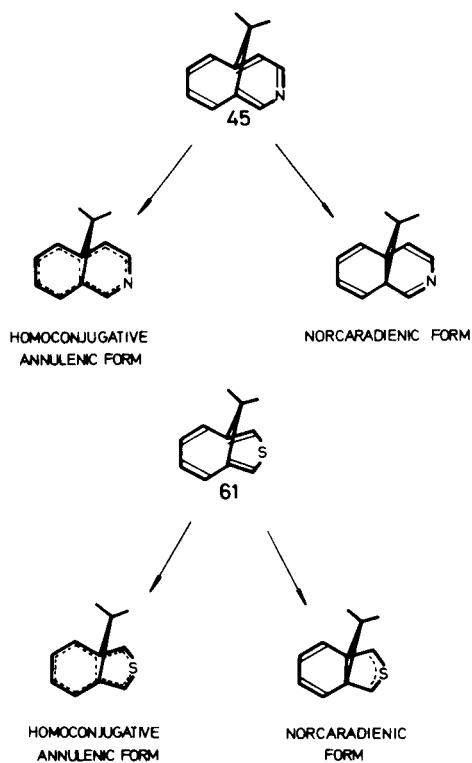

Figure 10.　The homoconjugative annulenic and norcara-dienic valence isomers of bridged aza[10]annulene (**45**) and bridged thionin (**61**).

Many of the studied systems, in spite of being feasible by the aromaticity criterion, have not yet been made be-cause of their high readiness to react.

REFERENCES AND NOTES

[1] Permanent address: The Rugjer Bošković Institute, P.O.B. 1016, 41001 Zagreb, Croatia, Yugoslavia.

[2] F. Sondheimer, *Pure Appl. Chem.*, **7**, 363 (1963).

[3] F. Sondheimer, I. C. Calder, J. A. Elix, Y. Gaoni, P. J. Garratt, K. Grohman, G. di Mayo, J. Mayer, M. V. Sargent and R. Wolovsky, *Spec. Publ.-Chem. Soc.*, No. 21, 75 (1967).

[4] F. Sondheimer, in "Proceedings of the Robert A. Welch Foun-dation Conference on Chemical Research. XII. Organic Synthesis", W. O. Milligan, ed, Houston, TX, 1968, p 125.

[5] F. Sondheimer, *Acc. Chem. Res.*, **5**, 81 (1972).

[6] F. Sondheimer, *Chimia*, **28**, 163 (1974).

[7] E. Vogel, *Spec. Publ. - Chem. Soc.*, No. 21, 113 (1967).

[8] E. Vogel, in "Proceedings of the Robert A. Welch Foundation Conference on Chemical Research. XII. Organic Synthesis", W. O. Milligan, ed, Houston, TX, 1968, p 215.

[9] E. Vogel, *Israel J. Chem.*, **20**, 215 (1980).

[10] E. Vogel, *Pure Appl. Chem.*, **54**, 1015 (1982).

[11] J. E. Lennard-Jones, *Proc. Roy. Soc. (London)*, **A 158**, 280 (1937).

[12] H. C. Longuet-Higgins and L. Salem, *ibid.*, **A 251**, 172 (1959); *ibid.*, **A 257**, 445 (1960).

[13] O. E. Polansky, *Monatsh. Chem.*, **91**, 916 (1960).

[14] M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.*, **87**, 685 (1965).

[15] N. Trinajstić and R. J. Wratten, *J. Mol. Struct.*, **3**, 395 (1969).

[16] J. Kruszewski and T. M. Krygowski, *Tetrahedron Letters*, 319 (1970).

[17] I. Gutman, M. Milun and N. Trinajstić, *Croat. Chem. Acta*, **44**, 207 (1972).

[18] N. L. Allinger and J. T. Sprague, *J. Am. Chem. Soc.*, **95**, 3893 (1973).

[19] A. Gavezzoti and M. Simonetta, *Helv. Chem. Acta*, **59**, 2984 (1976).

[20] I. Gutman, M. Milun and N. Trinajstić, *Croat. Chem. Acta*, **49**, 441 (1977).

[21] G. L. Grunewald, I. M. Uwaydah, R. C. Christofferesen and D. Spangler, *Tetrahedron Letters*, 933 (1979).

[22] A. Sabljić and N. Trinajstić, *J. Org. Chem.*, **46**, 3457 (1981).

[23] G. Favini, M. Simonetta, M. Sottocornola and R. Todeschini, *J. Chem. Phys.*, **74**, 3953 (1981).

[24] W. C. Herndon and C. Párkányi, *Tetrahedron*, **38**, 2551 (1982).

[25] L. Farnell and L. Radom, *J. Am. Chem. Soc.*, **104**, 1650 (1982).

[26] G. Favini, M. Simonetta and R. Todeschini, *J. Phys. Chem.*, **78**, 1895 (1983).

[27] A. G. Anastassiou, *Acc. Chem. Res.*, **5**, 281 (1972).

[28] G. Schröder, G. Frank and J. F. M. Oth, *Angew. Chem.*, **85**, 353 (1973).

[29] A. G. Anastassiou, in "Topics in Non-Benzenoid Aromatic

Chemistry'', T. Nozoe, R. Breslow, K. Hafner, S. Ito and I. Murata, eds, Vol I, John Wiley, New York, 1973, p 1.

[30] A. G. Anastassiou, *Pure Appl. Chem.*, **44**, 691 (1975).

[31] A. G. Anastassiou and H. S. Kasmai, *Adv. Heterocycic Chem.*, **23**, 55 (1978).

[32] E. Vogel, Lecture at the IUPAC International Symposium on Aromaticity, Dubrovnik, Croatia, September 3-5, 1979.

[33] J. W. Waluk, E. Vogel and J. Michl, *J. Org. Chem.*, **46**, 3306 (1981).

[34] M. Schäfer-Ridder, A. Wagner, M. Schwamborn, H. Schreiner, E. Devrout and E. Vogel, *Angew. Chem.*, **90**, 894 (1978).

[35] M. L. Maddox, J. C. Martin and J. C. Muchowski, *Tetrahedron Letters*, 7 (1980).

[36] R. J. Hunadi and G. K. Helmkamp, *J. Org. Chem.*, **46**, 2880 (1981).

[37] G. Hilken, T. Knikel, M. Schwamborn, J. Lex, H. Schmickler and E. Vogel, *Angew. Chem. Suppl.*, 1622 (1982).

[38] H. Kato and S. Toda, *J. Chem. Soc., Chem. Commun.*, 510 (1982).

[39] H. Kato, Private communication (April, 1983).

[40] I. Gutman, M. Milun and N. Trinajstić, *Math. Chem.* (Mülheim/Ruhr), **1**, 171 (1975).

[41] J.-i. Aihara, *J. Am. Chem. Soc.*, **98**, 2750 (1976).

[42] I. Gutman, M. Milun and N.Trinajstić, *ibid.*, **99**, 1962 (1977).

[43] K. Lammertsma, *ibid.*, **104**, 2070 (1982).

[44] The homoaromatic model for the bridged annulenes in not generally accepted. See for example, L. A. Paquette, *Angew. Chem.*, **90**, 114 (1978).

[45] H.-R. Blattmann, W. A. Böll, E. Heilbronner, G. Hohlneicher, E. Vogel and J.-P. Weber, *Helv. Chim. Acta*, **49**, 2017 (1966).

[46] W. Grimme, E. Heilbronner, G. Hohlneicher, E. Vogel and J.-P. Weber, *ibid.*, **51**, 225 (1968).

[47] P. Bischof, R. Gleiter and E. Heilbronner, *ibid.*, **53**, 1425 (1970).

[48] E. Heilbronner, in ''Aromticity, Pseudo-Aromaticity, Anti-Aromaticity'', E. D. Bergman and B. Pullman, eds, The Israel Academy of Sciences and Humanities, Jerusalem, 1971, p 58.

[49] R. Boschi, W. Schmidt and J.-C. Gfeller, *Tetrahedron Letters*, 4107 (1972).

[50] C. Batich, E. Heilbronner and E. Vogel, *Helv. Chim. Acta*, **57**, 2288 (1974).

[51] H. B. Burgi, E. Shefter and J. Dunitz, *Tetrahedron*, **31**, 3089 (1975).

[52] G. L. Grunewald and I. M. Uwaydah, *Tetrahedron Letters*, 933 (1975).

[53] J. Kolc, J. Michl and E. Vogel, *J. Am. Chem. Soc.*, **98**, 3935 (1976).

[54] R. C. Haddon, *J. Org. Chem.*, **42**, 2017 (1977).

[55] M. Simonetta, *Pure Appl. Chem.*, **52**, 1597 (1980).

[56] H. J. Dewey, H. Deger, W. Frölich, B. Dick, K. A. Klingensmith, G. Hohlneicher, E. Vogel and J. Michl, *J. Am. Chem. Soc.*, **102**, 6412 (1980); see also K. A. Klingensmith, W. Püttmann, E. Vogel and J. Michl., *ibid.*, **105**, 3375 (1983).

[57] H.-D. Martin and B. Mayer, *Angew. Chem., Int. Ed. Engl.*, **22**, 283 (1983).

[58] I. Gutman and N. Trinajstić, *Acta Chim. Acad. Sci. Hung.*, **91**, 203 (1976).

[59] N. Trinajstić, *Int. J. Quantum Chem.*, **S 11**, 469 (1977).

[60] I. Gutman, *Theoret. Chim. Acta*, **56**, 98 (1980).

[61] E. Heilbronner, *Chem. Phys. Letters*, **85**, 377 (1982).

[62] P. Ilić, B. Mohar, J. V. Knop, A. Jurić and N. Trinajstić, *J. Heterocyclic Chem.*, **19**, 625 (1982).

[63] J.-i. Aihara, *J. Am. Chem. Soc.*, **99**, 2048 (1977).

[64] P. Ilić and N. Trinajstić, *Croat. Chim. Acta*, **53**, 587 (1980).

[65] P. Ilić and N. Trinajstić, *ibid.*, **53**, 591 (1980).

[66] P. Ilić and N. Trinajstić, *J. Org. Chem.*, **45**, 1738 (1980).

[67] P. Ilić and N. Trinajstić, *Pure Appl. Chem.*, **52**, 1495 (1980).

[68] B. M. Gimarc and N. Trinajstić, *Inorg. Chem.*, **21**, 21 (1982).

[69] N. Trinajstić, ''Chemical Graph Theory'', CRC Press, Boca Raton, Florida, 1983.

[70] A. Stollenwerk, B. Kanellakopulos, H. Vogler, A. Jurić and N. Trinajstić, *J. Mol. Struct.*, in press.

[71] E. Heilbronner, Discussion after the lecture by E. D. Bergman and I. Agranat at the International Symposium on Aromaticity, Pseudo-Aromaticity, Anti-Aromaticity, Jerusalem, March 31-April 3, 1970, which is published, see ref 48, p 21; see also K. Fukui, *Science*, **218**, 747 (1982).

[72] I. Agranat, in ''Aromatic Compounds'', MTP International Review of Science, H. Zollinger, ed, Butterworths, London, 1973, p 139.

[73] W. Baker, in ''Perspectives in Organic Chemistry'', Sir Alexander Todd, ed, Interscience, New York, 1956, p 28.

[74] D. P. Craig, in ''Non-Benzenoid Aromatic Compounds'', D. Ginsburg, ed, Interscience, New York, 1953, p 1.

[75] G. M. Badger, in ''Aromatic Character and Aromaticity'', University Press, Cambride, 1969.

[76] M. J. S. Dewar, in ''The Molecular Orbital Theory of Organic Chemistry'', McGraw-Hill, New York, 1969, Chapter 5.

[77] P. J. Garratt, ''Aromaticity'', McGraw-Hill, New York, 1971.

[78] D. Lewis and D. Peters, ''Facts and Theories of Aromaticity'', MacMillan, London, 1975.

[79] J. V. Murrell, S. F. A. Kettle and J. M. Tedder, ''The Chemical Bond'', John Wiley, Chichester, 1979, second printing, Section 14.7.

[80] P. J. Garratt, ''Comprehensive Organic Chemistry'', J. F. Stoddart, ed, Vol 1, Pergamon, Oxford, 1979, p 215.

[81] L. J. Schaad and B. A. Hess, Jr., *Pure Appl. Chem.*, **54**, 1097 (1982).

[82] J. V. Knop and N. Trinajstić, *Int. J. Quantum. Chem.*, **S14**, 503 (1980).

[83] B. Mohar and N. Trinajstić, *J. Comput. Chem.*, **3**, 28 (1982).

[84] P. Ilić, B. Džonova-Jerman-Blažič, B. Mohar and N. Trinajstić, *Croat. Chem. Acta*, **52**, 35 (1979).

[85] N. Trinajstić, *ibid.*, **49**, 593 (1977).

[86] B. A. Hess, Jr., L. J. Schaad and C. W. Holyoke, Jr., *Tetrahedron*, **28**, 3657 (1972).

[87] B. A. Hess, Jr. and L. J. Schaad, *J. Am. Chem. Soc.*, **95**, 3907 (1973).

[88] B. A. Hess, Jr., L. J. Schaad and C. W. Holyoke, Jr., *Tetrahedron*, **31**, 295 (1975).

[89] H. Röttele and G. Schröder, *Angew. Chem., Int. Ed. Engl.*, **19**, 207 (1980).

[90] W. Gilb and G. Schröder, *ibid.*, **18**, 312 (1979).

[91] G. Jones, ''Quinolines'', G. Jones, ed, Part I, John Wiley, London, 1977, p 93.

[92] W. C. Herndon and C. Párkányi, *Tetrahedron*, **34**, 3419 (1978).

[93] P. Ilić, B. Sinković and N. Trinajstić, *Israel J. Chem.*, **20**, 258 (1980).

[94] S. Masamune and R. T. Seidner, *J. Chem. Soc., Chem. Commun.*, 542 (1969).

[95] F. Sondheimer, *Proc. Roy. Soc. (London)*, **A 297**, 173 (1967).

[96] R. M. McQuilkin, B. W. Metcalf and F. Sondheimer, *J. Chem. Soc. D*, 338 (1971).

[97] International Tables for X-Ray Chrystallography, Vol III, Physical and Chemical Tables, C. H. MacGilavry and G. D. Rieck, eds, The International Union of Chrystallography, The Kynoch Press, Birmingham, England, 1968, p 276.

[98] A. P. Bindra, J. A. Elix, P. J Garratt and R. H. Mitchell, *J. Am. Chem. Soc.*, **90**, 7372 (1968).

[99] G. Schröder, G. Frank and J. F. M. Oth, *Angew. Chem.*, **85**, 353 (1973).

[100] G. Schröder, *Pure Appl. Chem.*, **44**, 925 (1975).

[101] M. J. S. Dewar and T. Morita, *J. Am. Chem. Soc.*, **91**, 796 (1969).

[102] W. Königs, *Ber.*, **12**, 453 (1879); *ibid.*, **13**, 911 (1880).

[103] S. Hoogewerff and W. A. van Dorp, *Rec. Trav. Chim.*, **4**, 125 (1885); *ibid.*, **4**, 285 (1885).

[104] C. V. Wilson, in ''Six-Membered Heterocyclic Nitrogen

Compounds with Three Condensed Rings", L. F. H. Allen, ed, Interscience, New York, 1958, p 14.

[105] G. Koller and E. Strang, *Monatsh. Chem.*, **50**, 48 (1928).

[106] E. R. Webster, in "Six-Membered Heterocyclic Nitrogen Compounds with Four Condensed Rings", C. F. H. Allen, ed, Interscience, New York, 1951, p 3.

[107] A. Albert, D. J. Brown and H. Duewell, *J. Chem. Soc.*, 2028 (1948).

[108] F. Ullmann and I. C. Dasgupta, *Chem. Ber.*, **47**, 553 (1914).

[109] A. Pecault, *Bull. Soc. Chim. France*, 1270 (1950).

[110] M. J. Tanga and E. J. Reist, *J. Org. Chem.*, **47**, 1365 (1982).

[111] M. J. Hear and S. L. Swanson, *J. Heterocyclic Chem.*, **18**, 207 (1981).

[112] K. Burger, S. Tremmel, W.-D. Roth and H. Goth, *ibid.*, **18**, 247 (1981).

[113] R. K.-Y. Zee-Cheng and C. C. Cheng, *J. Med. Chem.*, **18**, 66 (1975).

[114] D. L. Boger, C. E. Brotherton and M. D. Kelley, *Tetrahedron*, **37**, 3977 (1981).

[115] L. P. Walls, in "Heterocyclic Compounds", Vol 4, R. C. Elderfield, ed, John Wiley, New York, 1952, p 564.

[116] N. R. Raulins, in "Acridines", R. M. Acheson, ed, John Wiley, New York, 1973, Second Ed, p 9.

[117] N. Trinajstić, *Rec. Chem. Progr.*, **32**, 85 (1971).

[118] L. Klasinc, E. Pop, N. Trinajstić and J. V. Knop, *Tetrahedron*, **28**, 3465 (1972).

[119] A. Baeyer, *Ann. Chem.*, **140**, 295 (1866).

[120] A. G. Perkin, *J. Chem. Soc.*, **23**, 368 (1870); *ibid.*, **24**, 295 (1871).

[121] L. Gattermann and A. E. Lockhart, *Chem. Ber.*, **26**, 2808 (1893).

[122] R. N. Warrener, *J. Am. Chem. Soc.*, **93**, 2346 (1971).

[123] R. Kreher and J. Seubert, *Z. Naturforsch.*, **20b**, 75 (1965).

[124] I. A. Carpino and D. E. Barr, *J. Org. Chem.*, **31**, 764 (1966).

[125] R. Mayer, H. Kleinert, S. Richter and K. Ewald, *Angew. Chem.*, **74**, 118 (1962).

[126] P. Demerseman, N. P. Buu-Hoi and R. Royer, *J. Chem. Soc.*, 4193 (1954).

[127] J. E. Shields and J. Bornstein, *Chem. Ind. (London)*, 1404 (1967).

[128] D. W. H. MacDowell, A. T. Jeffries and M. B. Meyers, *J. Org. Chem.*, **36**, 1416 (1971).

[129] Y. Tominaga, M. L. Lee and R. N. Castle, *J. Heterocyclic Chem.*, **18**, 967 (1981).

[130] M. P. Cava and J. P. Van Meter, *J. Org. Chem.*, **34**, 538 (1969).

[131] H.-J. Golz, J. Muchowski and M. L. Maddox, *Angew. Chem.*, **90**, 896 (1978).

[132] W. J. Lipa, H. T. Crawford, P. C. Radlick and G. H. Helmkamp, *J. Org. Chem.*, **43**, 3813 (1978).

[133] M. L. Maddox, J. C. Martin and J. C. Muchowski, *Tetrahedron Letters*, **21**, 7 (1980).

[134] Immediately after receiving a first draft of the present paper in mid April 1983, Professor H. Kato (Asashi, Matsumoto, Japan) informed us (April 22nd, 1983) that he has already prepared an eleven-π-electron bridged hetero[10]annulenone (3,10-diphenyl-4,9-methano-thiecin-2-one) [135] and that he is currently working on various other kinds of bridged heteroannulenes. Professor Kato concluded on the basis fo nmr data that the delocalisation of π electron in the above hetero-[10]annulene is only moderate. The TRE model (TRE(PE) = 0.005) supports these experimental findings.

[135] H. Kato, Y. Arikawa, M. Hashimoto and M. Masuzawa, *J. Chem. Soc., Chem. Commun.*, 938 (1983).

Note Added in Proof.

While the present paper was submitted to this Journal and was referred, we learned that Professor Renji Okazaki (Department of Chemistry, University of Tokyo, Tokyo, Japan) reported bridged thionin **58**. In his personal communication to us (September 2, 1983) Professor Okazaki described **58** as an aromatic compound. In addition, he informed us about his attempt to prepare **57**. We are thankful to Professor Okazaki for correspondence and information about his work on bridged azonine **57** and bridged thionin **58**.