

Aromatic Stability of Bridged Annulenes¹

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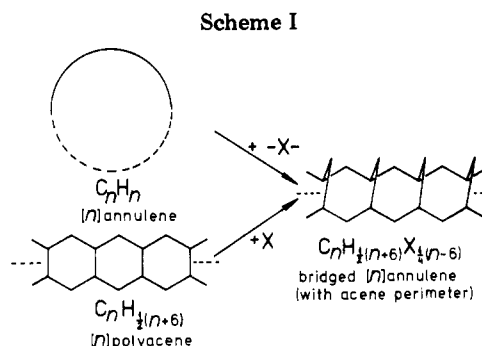
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The aromatic stability of methano-bridged [*n*]annulenes (with *n* up to 30) and their mono- and diions was studied by means of the topological resonance energy approach. Methano-bridged [*n*]annulenes are predicted to be aromatic, radical ions of lower bridged annulenes to be nonaromatic, and those of higher ones to be aromatic, while in the case of diions the aromatic stability increases with the size of a molecule from antiaromatic through nonaromatic to aromatic. Experimental evidence only partially supports the theoretical results.

In parallel to the preparation of [*n*]annulenes by Sondheimer's group,²⁻⁶ Vogel, Boekelheide, and others have prepared various types of bridged [*n*]annulenes.⁷⁻¹⁰ Here we are interested in the class of the bridged [*n*]annulenes, with $n = (4m + 2)$ [$m = 1, 2, \dots$] π electrons, which may be formally derived from linear [*n*]polyacenes by insertion of an atom or a group X (X = O, S, NH, CH₂, etc.) into the bonds common to two rings. Alternatively, the bridged [*n*]annulenes may also be formally constructed from [*n*]annulenes by inserting the bridge X between appropriate sites on the annulene ring. This may be illustrated as shown in Scheme I.

Because of the proximity of the two bridged sites on the annulene perimeter, there is a considerable homoaromatic interaction across the molecule at the bridged ends.¹¹⁻¹⁴ One may conjecture that the weaker (stronger) the transannular interaction in the bridge structure, the closer is its similarity to the corresponding annulene (polyacene).

Preparative efforts in the chemistry of annulenes and bridged annulenes contributed to the understanding of the Hückel ($4m + 2$) rule according to which monocyclic systems are aromatic if they contain $(4m + 2)$ π electrons and are planar. However, the Hückel rule is qualitative and says nothing about the effect of ring size on the stability of the annulene system. It is known that, at certain size, the Hückel rule breaks down;¹⁵⁻¹⁸ i.e., the $(4m + 2)$ an-



nulene system becomes a nonaromatic structure contrary to the original Hückel prediction.¹⁹

Here we investigate the aromatic stability of methano-bridged annulenes (with *n* up to 30) in the same way as we studied the stability of annulenes¹⁸ using the topological resonance energy (TRE) model.²⁰⁻²² The TRE model has shown to be very reliable for predicting aromaticity in hydrocarbons,^{21,22} heterocycles,²¹⁻²⁴ conjugated ions and radicals,²⁵ homoaromatic structures,²⁶ and conjugated molecules in the lowest electronic excited states.²⁷

The numerical work is carried out by using eq 1, where

$$\text{TRE} = \sum_{j=1}^n g_j(x_j - x_j^{\text{ac}}) \quad (1)$$

x_j 's are the Hückel eigenvalues, while x_j^{ac} 's are those of the acyclic (matching) polynomials. The acyclic polynomial is used in the TRE model to represent the Dewar-type acyclic reference structure,²⁰ and its computation is described elsewhere.^{20,28-30} TRE may be interpreted as the degree of aromatic stabilization of a cyclic conjugated system in the ground state. It is equal to the difference between the total π -electron energy of a conjugated molecule and the total π -electron energy that the conjugated molecule would possess in the ground state if it were absolutely olefinic in nature.

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(13) The homoaromatic model for the bridged annulenes is not generally accepted. See, for example, L. A. Paquette, *Angew. Chem.*, **90**, 114 (1978). The origin of this uncertainty is perhaps due to dependence on the results of the NMR measurements alone in detecting the homoaromatic interactions. However, the NMR data are not a reliable source for diagnosing the transannular interactions because they are not essential for continuation of cyclic conjugation.^{11,14}

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Table I. TRE and TRE(PE) Values of Bridged $[n]$ Annulenes and the Corresponding $[n]$ Annulenes and $[n]$ Polyacenes

$[n]$	$[n]$ polyacenes		bridged $[n]$ annulenes			$[n]$ annulenes		
	TRE ^a	TRE(PE)	TRE	TRE(PE)	ref to prep work	TRE ^b	TRE(PE)	ref to prep work
[10]	0.389	0.039	0.291	0.029	<i>c</i>	0.159	0.016	<i>g</i>
[14]	0.475	0.034	0.320	0.023	<i>d</i>	0.113	0.008	<i>h</i>
[18]	0.553	0.031	0.350	0.019	<i>e</i>	0.088	0.005	<i>i</i>
[22]	0.626	0.028	0.382	0.017	<i>f</i>	0.072	0.003	<i>j</i>
[26]	0.706	0.027	0.425	0.016		0.061	0.002	<i>k</i>
[30]	0.783	0.026	0.469	0.016		0.052	0.002	<i>l</i>

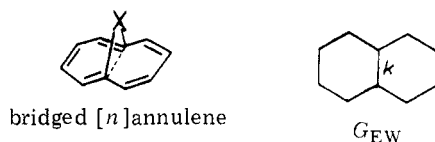
^a I. Gutman, M. Milun, and N. Trinajstić, *J. Am. Chem. Soc.*, **99**, 1692 (1977); J.-i. Aihara, *ibid.*, **99**, 2048 (1977). ^b P. Ilić, B. Sinković, and N. Trinajstić, *Isr. J. Chem.*, **20**, 258 (1980). ^c E. Vogel and H. D. Roth, *Angew. Chem., Int. Ed. Engl.*, **3**, 228 (1964). ^d E. Vogel, J. Sombroek, and W. Wagemann, *Angew. Chem.*, **87**, 591 (1975). ^e W. Wagemann, M. Iyoda, H. M. Deger, J. Sombroek, and E. Vogel, *ibid.*, **90**, 988 (1978). ^f Private communication from Professor E. Vogel. ^g S. Masamune and R. T. Seidner, *Chem. Commun.*, 542 (1969). ^h F. Sondheimer, *Proc. R. Soc. London Ser. A*, **297**, 173 (1967). ⁱ F. Sondheimer, *Pure Appl. Chem.*, **7**, 363 (1963). ^j R. M. McQuilkin, B. W. Metcalf, and F. Sondheimer, *J. Chem. Soc. D*, 338 (1971). ^k B. W. Metcalf and F. Sondheimer, *J. Am. Chem. Soc.*, **93**, 5271 (1971). ^l M. Iyoda and M. Nakagawa, *Tetrahedron Lett.*, 4743 (1973).

In order to compare molecules of various size, TRE is normalized^{20,31} by eq 2, where TRE(PE) stands for TRE

$$\text{TRE(PE)} = \frac{\text{TRE}}{n} \quad (2)$$

per π electron, while n is the number of π electrons in the conjugated system. The threshold values for classifying conjugated systems are as follows: (a) molecules with $\text{TRE(PE)} > 0.01$ are considered aromatic, (b) molecules with TRE(PE) values between -0.01 and $+0.01$ are non-aromatic, and (c) molecules with $\text{TRE(PE)} < -0.01$ are antiaromatic and unstable.

The bridged $[n]$ annulenes are represented by the edge-weighted graphs,³² G_{EW} .



The magnitude of the homoaromatic interaction across the ring is denoted by the edge (bond) with "weight" k .^{26,33} Since the homoaromatic parameter k is a crucial quantity in our calculations we have varied it from 0.00 ([10]-annulene) to 1.00 (naphthalene). As an example, the TRE of 1,6-methano[10]annulene as a function of k is plotted in Figure 1.

We see that the TRE variation is smooth from annulene to polyacene. This is observed in all cases studied. Thus, depending on the value of k , the bridged structures are either similar to annulenes ($k \rightarrow 0.00$) or similar to polyacenes ($k \rightarrow 1.00$). The value of parameter k is, of course, unknown, but we selected $k = 0.4$, following the suggestion by Hohlneicher.³⁴ This value is deduced from an analysis of spectral data (optical spectra, photoelectron spectra, polarized fluorescence, magnetic circular dichroism)^{11,35-39} which point out that the transannular interaction is rather

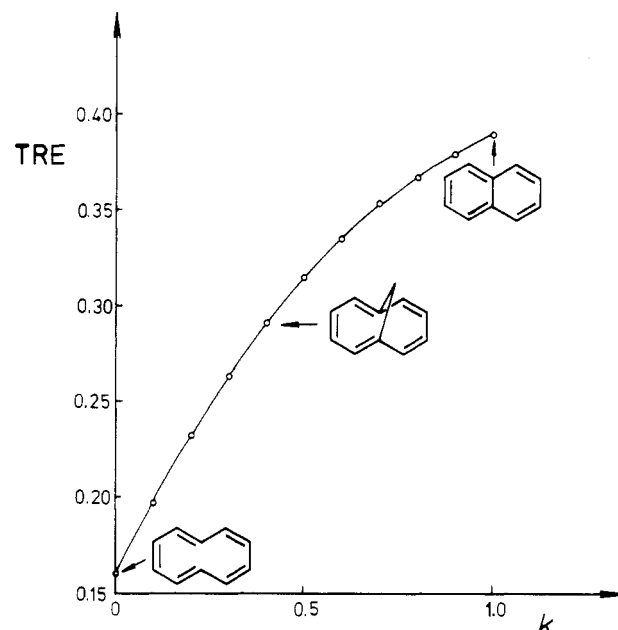


Figure 1. TRE vs. parameter k for 1,6-methano[10]annulene.

strong in the bridged structures. Matching of this value ($k = 0.4$) with the calculations reported in Figure 1 produces the TRE value of 1,6-methano[10]annulene ($\text{TRE} = 0.291$; $\text{TRE(PE)} = 0.029$) which places this molecule in the class of aromatic species. This prediction is in agreement with the experimental facts.⁹

However, we are quite aware that by assuming that the bridged structures are planar and that the only effect in operation within the system is the homoaromatic interaction, we have oversimplified the physical picture of the bridged annulene. In fact, the perturbed perimeter of the bridged structure is not in reality planar.⁴⁰ The degree of nonplanarity of the annulene perimeter depends on the bridging groups. Sometimes different types of bridges will produce systems with like perimeters. This is the case with *syn*-1,6:8,13-dimethano[14]annulene (**1**) and 1,6:8,13-propane-1,3-diylidene[14]annulene (**2**) where X-ray data show the perimeters to be virtually identical.^{41,42}



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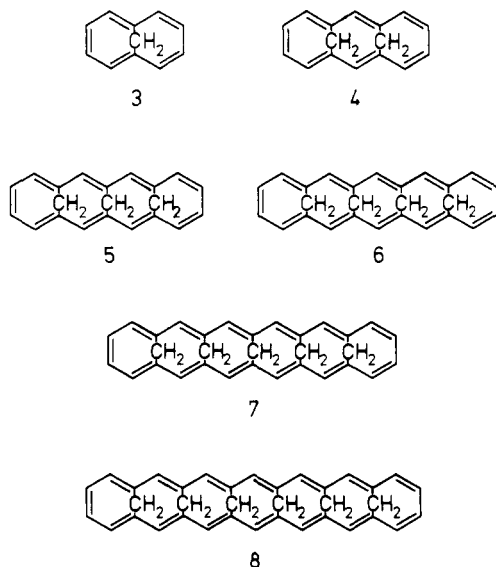


Figure 2. Schematic representation of the bridged $[n]$ annulenes studied.

The schematic representation of the series of methano-bridged $[n]$ annulenes with $n = 10$ up to $n = 30$, studied in the present work, is given in Figure 2.

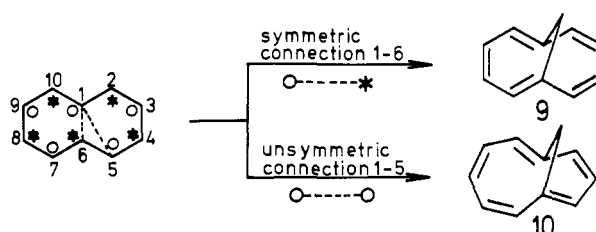
The TRE and TRE(PE) values of systems 3–8 are given in Table I.

Table I also contains a comparison between the methano-bridged annulenes and the corresponding $[n]$ annulenes and $[n]$ polyacenes. All six planar bridged annulenes studied are predicted to be aromatic structures, since their values of TRE(PE) are larger than 0.01. The bridged [10]-, [14]-, and [18]annulenes have been prepared,^{43–45} bridged [22]annulene has also been prepared but is still under investigation,⁴⁶ while bridged [26]annulene and [30]annulene are not known as yet. The predicted aromatic character in this series drops from 63% of that of benzene in bridged [10]annulene to 35% in the bridged [30]annulene. Since there are increasing difficulties in preparing the higher bridged annulenes,⁴⁶ which are also a matter of synthetic methodology and need not be tied exclusively to the properties of these compounds, their aromatic stability must be a result of a complicated interplay of conformational, inductive, conjugative, and homoaromatic effects. Besides, the additional stability of bridged annulenes when compared to simple annulenes does not come from homoaromatic interactions alone. Presumably, rigidity of the ring skeleton is also a factor since Boekelheide's bridged [14]annulenes,¹⁰ which should not exhibit pronounced homoaromatic interactions, fully match methano-bridged annulenes in stability.⁴⁷ This is experimentally verified, for example, by comparing the stability of the syn and anti configurations of bridged [14]annulene. The syn structure is much more stable than the anti.⁷ The reason for the instability of the anti configuration of bridged [14]annulene, which is a highly re-

active polyolefinic structure, is connected with the puckered rigid perimeter of this molecule.

Another interesting effect in operation in the bridged $[n]$ annulenes is related to the symmetry of placing the bridge. If the bridge is symmetrically placed, i.e., if it connects two atoms of different parity on the annulene perimeter, the bridged structure obtained should be more stable than the structure generated when the bridge is placed unsymmetrically, i.e., if it connects two atoms of the same parity.

Structure 9 is predicted to be more stable than 10. This prediction is based on the simple argument that the interaction between the positions of different parity is stabilizing, while in the opposite case it is destabilizing.^{48,49} This prediction is also supported by the TRE values, since TRE of 10 (0.155) is smaller for 43% than TRE of 9 (0.291). Structure 10 is, thus, predicted to be aromatic, but less stable than the related structure 9. Structure 10 indeed differs in its properties from structure 9.⁵⁰



The above prediction is also well supported by extensive studies on 10 by Scott and co-workers.^{51,52} They found that 10 resembles azulene in its physical and chemical properties and proposed the colloquial name "homoazulene" for it. The 3-methoxy derivative of 10 was found to be aromatic on the basis of NMR evidence and to be similar in its aromatic character to 9.

The corresponding polyacenes are also all predicted to be aromatic, though they differ in their degrees of aromaticity. This result is in accordance with other theoretical predictions^{53–55} and with the experimental findings.⁵⁶ However, the preparation of large polyacenes is rather difficult. The larger polyacenes become more and more instable toward Diels–Alder attack with increasing size.⁵⁶ This is in accord with the predictions based on the HOMO–LUMO separation which with the increasing size of polyacenes drops from 2.00 in benzene to only 0.27 in heptacene.⁵⁷ (These values are given in β units.) Therefore, polyacenes represent a class of aromatic molecules for which the thermodynamic stability gradually diminishes with increasing size while the reactivity (addition reactions, photooxidation) increases dramatically.

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Table II. TRE and TRE(PE) Values of Radical Ions of Bridged Systems 3-8

[n]	bridged [n]annulene radical ions			[n]annulene radical ions		
	TRE	TRE(PE)	predicted status	TRE	TRE(PE)	predicted status
[10] ⁺	-0.007	-0.001	NA	-0.145	-0.016	AA
[10] ⁻	-0.007	-0.001	NA	-0.145	-0.013	AA
[14] ⁺	0.120	0.001	NA	-0.109	-0.008	NA
[14] ⁻	0.120	0.001	NA	-0.109	-0.007	NA
[18] ⁺	0.208	0.012	A	-0.083	-0.005	NA
[18] ⁻	0.208	0.011	A	-0.083	-0.004	NA
[22] ⁺	0.276	0.013	A	-0.076	-0.004	NA
[22] ⁻	0.276	0.012	A	-0.076	-0.003	NA
[26] ⁺	0.346	0.014	A	-0.060	-0.002	NA
[26] ⁻	0.346	0.013	A	-0.060	-0.002	NA
[30] ⁺	0.409	0.014	A	-0.052	-0.0018	NA
[30] ⁻	0.409	0.013	A	-0.052	-0.0017	NA

Table III. TRE and TRE(PE) Values of Dications and Dianions of Bridged Systems 3-8

[n]	bridged [n]annulene diions				[n]annulene diions		
	TRE	TRE(PE)	predicted status	ref to prep work	TRE	TRE(PE)	predicted status
[10] ²⁺	-0.305	-0.038	AA		-0.450	-0.056	AA
[10] ²⁻	-0.305	-0.025	AA		-0.450	-0.038	AA
[14] ²⁺	-0.080	-0.007	NA		-0.330	-0.028	AA
[14] ²⁻	-0.080	-0.005	NA	<i>a</i>	-0.330	-0.021	AA
[18] ²⁺	0.066	0.004	NA	<i>b</i>	-0.256	-0.016	AA
[18] ²⁻	0.066	0.003	NA		-0.256	-0.013	AA
[22] ²⁺	0.170	0.009	NA		-0.218	-0.011	AA
[22] ²⁻	0.170	0.007	NA		-0.218	-0.009	NA
[26] ²⁺	0.267	0.011	A		-0.180	-0.0075	NA
[26] ²⁻	0.267	0.010	A		-0.180	-0.0064	NA
[30] ²⁺	0.349	0.012	A		-0.156	-0.0056	NA
[30] ²⁻	0.349	0.011	A		-0.156	-0.0049	NA

^a F. Gerson, K. Müllen, and E. Vogel, *Angew. Chem.*, **83**, 1014 (1971). ^b H. M. Deger, K. Müllen, and E. Vogel, *ibid.*, **90**, 990 (1978).

Thus, the TRE value of heptacene is equal to 67% of the TRE value of benzene, while the HOMO-LUMO separation is equal to only 14% of that in benzene. Therefore, it is not a surprise that heptacene undergoes an addition reaction with maleic anhydride rather easily.⁵⁸

Another problem which makes the preparation of large polyacenes so difficult is the very low solubility of these compounds which is also found for the last precursor in the synthetic route. All [n]annulenes studied, except [10]annulene, on the other hand, are predicted to be nonaromatic. [10]Annulene is classified as aromatic. This prediction is based on the planar skeleton of [10]annulene. However, in [10]annulene the repulsion between the inner hydrogen atoms is considerable and affects the planarity of the ring.⁵⁹

In order to test further our model we have also calculated positive and negative radical ions and diions of structures 3-8. These results are reported in Tables II and III.

All bridged annulene radical ions studied, except bridged [10]annulene and [14]annulene radical anions and radical cations, are predicted to be aromatic. Bridged [10]-annulene and [14]annulene radical ions are predicted to be nonaromatic. Unfortunately, the experimental data needed to test these predictions are not available. The corresponding [n]annulene radical ions are predicted to be antiaromatic ($n = 10$) and nonaromatic ($n = 14, 18, 22, 26, 30$). Here again no experimental data are available.

Bridged [n]annulene diions are predicted to be antiaromatic with $n = 10$, nonaromatic with $n = 14, 18$, and

22, and aromatic with $n = 26$ and 30. Here again hardly any experimental data are available. The only known compounds of this series are the bridged [14]annulene dianion and [18]annulene dication.^{60,61} They are both of low stability and exist only at low temperatures. The parallel [n]annulene diions are predicted to be antiaromatic ($n = 10, 14, 18$) and nonaromatic ($n = 26, 30$). The corresponding experimental data also are scarce. The only known dianion is that of [18]annulene which is found to be antiaromatic.⁶² This observation is in fine agreement with the predicted antiaromatic status of [18]annulene dianion.

Annulene diions were also studied by Hess and Schaad.⁶³ In these studies they have used their original aromaticity index, REPA (resonance energy per atom). Hess and Schaad predicted both dianions and dications of [n]-annulenes to be aromatic species. However, this theoretical result does not follow the Hückel rule according to which a change in π electrons in the annulene ring changes its aromaticity.⁶⁴ Since the [n]annulenes considered in the present work are of the $(4m + 2)$ type (the number of sites and π electrons being identical), their dianions and dications will be species with $4m$ π electrons on the $(4m + 2)$ periphery. They are expected to be antiaromatic for $m =$ small or nonaromatic for $m =$ large.⁶⁵ Our results and

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those of others³³ follow this trend.

The lack of experimental data for bridged $[n]$ annulene and $[n]$ annulene ions is indicative of the difficulties in attempting to prepare these species. This correlates well with our predictions of low aromatic stability which anticipate problems in making the annulene ions of both variety.

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Registry No. 3, 2443-46-1; 3 radical cation, 78037-43-1; 3 radical anion, 35533-21-2; 3 dication, 77984-15-7; 3 dianion, 77966-07-5; 4, 14458-51-6; 4 radical cation, 78085-70-8; 4 radical anion, 78085-71-9; 4 dication, 77966-08-6; 4 dianion, 77966-09-7; 5, 78038-55-8; 5 radical cation, 78038-56-9; 5 radical anion, 78037-44-2; 5 dication, 68630-17-1; 5 dianion, 77984-14-6; 6, 77965-99-2; 6 radical cation, 77966-00-8; 6 radical anion, 78037-45-3; 6 dication, 77966-10-0; 6 dianion, 77966-11-1; 7, 77966-01-9; 7 radical cation, 77966-02-0; 7 radical anion,

78037-46-4; 7 dication, 78018-23-2; 7 dianion, 77966-12-2; 8, 77966-03-1; 8 radical cation, 77966-04-2; 8 radical anion, 78037-47-5; 8 dication, 77966-13-3; 8 dianion, 77966-14-4; $[n]$ polyacene ($n = 10$), 91-20-3; $[n]$ polyacene ($n = 14$), 120-12-7; $[n]$ polyacene ($n = 18$), 92-24-0; $[n]$ polyacene ($n = 22$), 135-48-8; $[n]$ polyacene ($n = 26$), 258-31-1; $[n]$ polyacene ($n = 30$), 258-38-8; $[n]$ annulene ($n = 10$), 3227-76-7; $[n]$ annulene ($n = 14$), 2873-14-5; $[n]$ annulene ($n = 18$), 2040-73-5; $[n]$ annulene ($n = 22$), 3227-79-0; $[n]$ annulene ($n = 26$), 3332-39-6; $[n]$ annulene ($n = 30$), 3332-40-9; $[n]$ annulene ($n = 10$) dication, 59975-80-3; $[n]$ annulene ($n = 10$) dianion, 59947-29-4; $[n]$ annulene ($n = 14$) dication, 59975-82-5; $[n]$ annulene ($n = 14$) dianion, 77984-16-8; $[n]$ annulene ($n = 18$) dication, 77984-17-9; $[n]$ annulene ($n = 18$) dianion, 77984-18-0; $[n]$ annulene ($n = 22$) dication, 77984-19-1; $[n]$ annulene ($n = 22$) dianion, 77984-20-4; $[n]$ annulene ($n = 26$) dication, 77984-21-5; $[n]$ annulene ($n = 26$) dianion, 77984-22-6; $[n]$ annulene ($n = 30$) dication, 78003-76-6; $[n]$ annulene ($n = 30$) dianion, 77984-23-7; $[n]$ annulene ($n = 10$) radical cation, 78037-48-6; $[n]$ annulene ($n = 10$) radical anion, 78037-49-7; $[n]$ annulene ($n = 14$) radical cation, 78037-50-0; $[n]$ annulene ($n = 14$) radical anion, 78037-51-1; $[n]$ annulene ($n = 18$) radical cation, 78037-52-2; $[n]$ annulene ($n = 18$) radical anion, 78037-53-3; $[n]$ annulene ($n = 22$) radical cation, 77966-05-3; $[n]$ annulene ($n = 22$) radical anion, 78037-54-4; $[n]$ annulene ($n = 26$) radical cation, 77966-06-4; $[n]$ annulene ($n = 26$) radical anion, 78037-55-5; $[n]$ annulene ($n = 30$) radical cation, 78037-56-6; $[n]$ annulene ($n = 30$) radical anion, 78037-57-7.

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Reactions of Nitrosoureas and Related Compounds in Dilute Aqueous Acid: Transnitrosation to Piperidine and Sulfamic Acid

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The transnitrosation reactions of four classes of nitrosamides in dilute aqueous acid were studied. Trialkyl nitrosoureas and nitrosoguanidines were found to react very rapidly in transnitrosations to piperidine, giving high yields (70–90%) of nitrosopiperidine at pH 1.7 (perchloric acid) or pH 3.3 (formate buffer). Methylnitrosourea reacted more slowly than either the trialkylnitrosoureas or the nitrosoguanidines and gave moderate yields (48%) of nitrosopiperidine at pH 1.7 and low yields (6%) at pH 3.3. Nitrosourethanes gave high yields at pH 1.7 and moderate yields at pH 3.3. Denitrosation rates (transnitrosation to a nitrite trap) are given for a series of monoalkyl- and trialkylnitrosoureas. An increase in the size of the alkyl group at N_1 decreased the rate of denitrosation. The kinetics of nucleophile-catalyzed transnitrosation from trialkylnitrosoureas to piperidine at pH 1.7 for a series of four trialkylnitrosoureas have been studied. Both the denitrosation of the donor and the nitrosation of the recipient were studied with respect to thiocyanate ion concentration. The denitrosation step was affected only at high $[SCN^-]$, while the nitrosation step showed a first-order dependence on thiocyanate at most concentrations, with a "leveling off" effect observed at high $[SCN^-]$. The denitrosation step does not exhibit a true dependence on thiocyanate concentration but merely reflects the rapid rate of the nitrosation of the recipient piperidine at high $[SCN^-]$ as a consequence of mass action. The behavior of nitrosoureas in transnitrosation reactions is compared with that of alicyclic nitrosamines. The latter differ from nitrosoureas in that they react more slowly, require a nucleophilic catalysis at the denitrosation step, and do not always nitrosate strongly basic amines.

The ability of a nitrosamine to act as a nitrosating agent (i.e., to effect transnitrosation) has been demonstrated for aromatic nitrosamines,^{1,2} which can react via direct and indirect mechanisms, in organic and aqueous media.³ Many aliphatic nitrosamines will transnitrosate under mild conditions in dilute aqueous acid with nucleophilic catalysts.^{4,5}

Nitrosamides are less stable than nitrosamines in acid.⁶ While much is known about the potential alkylating ability of nitrosamides in base via alkyl diazonium ion formation, the acid hydrolysis reactions and, in particular, the nitrosating ability of nitrosoureas have received little attention. Challis and co-workers studied the denitrosation and deamination reactions of *N*-nitrosopyrrolidone⁷ and *N*-butyl-*N*-nitrosoacetamide,⁸ and Williams has studied the denitrosation reactions of 1-methyl-1-nitroso-*p*-toluenesulfonamide.⁹ In both cases, proton transfer from

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