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Stability and Resonance Energy of Troponoid Compounds[1)]

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The fundamental skeleton of the tropones possessing a unique heptagonal structure is predicted to be aromatic with positive resonance energies and conforming to the topological charge stabilization rule (TCS rule). Similarly, naturally occurring tropolones also nicely fit the theory that conformity to the TCS rule gives a stable molecular system. Thus, many of the troponoids so far synthesized and those occurring in nature are energetically very stable molecules as well as being synthetically very accessible. The TCS rule applies very well to the formation mechanism of heterocycle-fused tropones. It is very likely that there are various reaction paths in nature which are compatible with the TCS rule for the formatin of tropylium compounds having annulated heterocycles.

After structure elucidation of natural tropolones such as α-, β-, and γ-thujaplicins, colchicins, stipitatic acid, and its co-metabolic homologues, and purpurogallin, syntheses of many tropolones and tropones were achieved in the early 1950's.[2)]

Since then, extensive studies regarding various aspects eventually led to the establishment of a new field, the chemistry of nonbenzenoid aromatic compounds.[3)] It might be very important to seek the reason why these molecules are synthesized and occur in nature. What factors stabilize these rather peculiar molecules? Of course, it is not easy to answer this question. However, even a partial answer would represent important progress in the study of the chemistry of troponoid compounds.

In 1983 Gimarc pointed out that the pattern of charge densities in a molecule is determined primarily by its connectivity, or topology.[4a)] Many examples indicate that nature prefers to place heteroatoms of great electronegativity in positions where the isostructural, iso-π-electronic hydrocarbon has large charge densities.[4a–c)] Gimarc[4a–c)] referred to isostructural, iso-π-electronic hydrocarbons as a uniform reference frame (URF) and called "the effect the rule of topological charge stabilization," or the TCS rule. He showed[4a)] that the TCS rule cannot differentiate between the stabilities of aromatic, nonaromatic, and antiaromatic structures. On the other hand, Aihara[5)] developed a general graph theoretical formula for the resonance energy, circuit resonance energy,[5d)] and bond currents.[5k)] Many examples indicate that the graph theory of aromaticity has been one of the most important principles in the study of aromaticity. In this paper we describe both the stability and aromaticity of troponoids and annulated troponoids in terms of Gimarc's TCS rule and Aihara's graph theory of aromaticity.

More recently, Nozoe et al.[6)] synthesized tropylium compounds having tri-annulated heterocycles and related compounds. To obtain useful imformation about very complex reactions leading to the formation of these heterocyclic tropylium systems, we also describe the stability of the starting materials, intermediates, and products in terms of Gimarc's TCS rule.

The HMO theory is assumed in its simplest form. Streitwieser evaluated the heteroatom parameters for the amine nitrogen, the imine nitrogen, the ether oxygen, and the ketone oxygen.[7)] In this paper, we adopt these values with some other heteroatom parameters.[8,9)] Ketone oxygen, imine nitrogen, and thione sulfur contribute one π-electron to the conjugated system, whereas amine nitrogen, alcohol (or ether) oxygen, and thioether sulfur contribute two π-electrons instead of one.

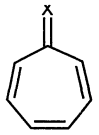
Results and Discussion

Monocyclic Troponoids. The calculated resonance energies and bond currents[5)] for a series of monocyclic troponoids are given in Table 1. Tropone (**1a**),

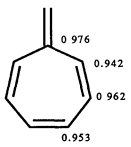
Table 1. Resonance Energies and Bond Currents of Monocyclic Troponoids

	Neutral species		Cationic species	
	RE	Bond current	RE	Bond current
1a	0.1776	0.9404	0.2163	1.1056
1b	0.1254	0.7077	0.2097	1.0823
1c	0.1518	0.8235	0.2025	1.0515
4a	0.1781	0.9357	0.2111	1.0846
4b	0.1748	0.9187	0.2058	1.0597
4c	0.1703	0.8967	0.1996	1.0325
5a	0.1305	0.7248	0.2058	1.0597
5b	0.1292	0.7152	0.2009	1.0364
5c	0.1258	0.6972	0.1951	1.0103
6a	0.1540	0.8277	0.1996	1.0325
6b	0.1517	0.6830	0.1951	1.0103
6c	0.1479	0.7952	0.1895	0.9845

RE: Resonance energy (in β unit). Bond current (in benzene, I_0, unit).



1a X=O
b X=NH
c X=S



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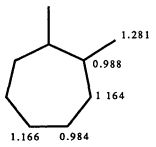

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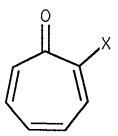
troponeimine (**1b**), and thiotropone (**1c**) have been prepared.[3]

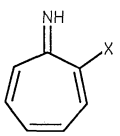
Heptafulvene[3] (**2**) is a URF for these compounds. This URF has the largest charge density at position 8. Compound **2** is predicted to be essentially polyolefinic in nature.[10] Though it has been prepared, it is too reactive to be isolated.[10] The resonance energy of **2** was calculated to be 0.009.[5a] In each compound recorded in Table 1 the heteroatom is located at the position of the maximum charge density in the URF. Compound **1a** is the most stable because oxygen is more electronegative than nitrogen and sulfur.[11] Compounds **1a—c** are predicted to be aromatic, with positive resonance energies. Among them, the resonance energy for **1a**[5a] is largest. Compound **1b** is rather unstable and removal of the solvent from its solution causes immediate polymerization. Compound **1c** is also very unstable in solution. It appears to form a mercaptotropylium ion in concentrated sulfuric acid.[12]

Though troponeiminium salts are stable in air and in a neutral or acidic aqueous solution, they are rapidly hydrolyzed by aqueous alkali.[13] The ^{1}H NMR spectrum of the troponeiminium salts with peaks at δ=6.3 indicates an upfield shift of the ring-proton signals from those of **1a** by 0.6 ppm.[14] As shown in Table 1, compound **1b** has small calculated bond currents in agreement with its chemical shift.

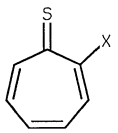
We next consider the URF of the 1-methyleneheptafulvene anion (**3**). Here, the largest charge densities are at the *exo*-methylene carbons. The iso-π-electronic molecules tropolone (**4a**), 2-aminotropone (**4b**), and 2-mercaptotropone (**4c**) are all stable compounds.[3]



4a X=OH
b X=NH$_2$
c X=SH



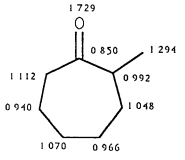
5a X=OH
b X=NH$_2$
c X=SH



6a X=OH
b X=NH2
c X=SH

Compound **3** is a URF for these compounds. In each case, the oxygen atom is located at one of the *exo*-methylene carbons and the substituent is located at the other *exo*-methylene carbons of maximum charge in the URF **3**.

Similarly, the iso-π-electronic molecules, **5a—c** and **6a—c**, are all stable compounds.[3] Compound **3** is also a URF for **5** and **6**. In each case the heteroatoms and the substituents are located at the sites of the largest charge density in the URF **3**. Then, starting from the stability of **1a—c**, we consider the stability of the 1-methylenetropone anion (**7**) and its *N*- (**8**) and *S*-analogue (**9**). In all cases, the largest charge density is



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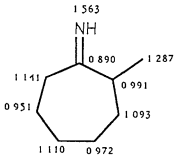

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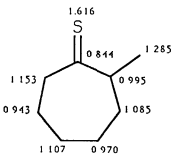

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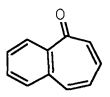
at the *exo*-methylene carbons. Compounds **4**, **5**, and **6** can also be designed by replacing the *exo*-methylene carbon by the iso-π-electronic substituents. It has therefore become evident that tropones and tropolones conform to the TCS rule. Most heteroatoms and iso-π-electronic substituents are placed at the sites of large charge density in the URF. As shown in Table 1, all monocyclic troponoids are predicted to be aromatic with positive resonance energies. Their cationic species have larger resonance energies and bond currents than do the neutral species.

Benzotropones. Unlike tropones, tropone-annulated benzenoids show different reactivities from those shown by tropone itself.[3] As a measure of the characteristics of tropone, Table 2 compares the calculated circuit resonance energies contributed by the seven-membered ring (r_2) to benzotropones.

Among them, tribenzotropone (**24**) has a small circuit resonance energy. The relative values of the circuit resonance energies for these benzotropones decrease with the number of benzene rings. Three isomeric benzotropones **10—12** are known, among which **10** and **12** have been isolated; **11** has not been



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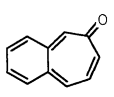

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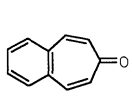

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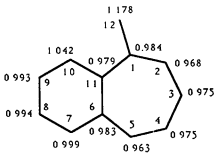
Table 2. Resonance Energies, Circuit Resonance Energies, and Bond Currents of Benzotropones

	RE	REPE	r_2	Bond currents
10	0.3132	0.0261	0.0576	0.8606
11	0.2840	0.0237	0.0721	1.1045
12	0.3087	0.0257	0.0577	0.9632
16	0.4136	0.0258	0.0293	1.0296
17	0.4253	0.0266	0.0299	1.0837
18	0.4768	0.0298	0.0217	0.7124
19	0.4852	0.0303	0.0207	0.6823
24	0.6817	0.0341	0.0075	0.5007

RE: Resonance energy (in β unit). REPE: Resonance energy per π-electron. Bond current (in benzene, I_0, unit).

prepared yet.[15] The charge densities of the corresponding URF's (**13**, **14**, and **15**) reveal that the oxygen atom in each isomer occupies the sites of the largest charge density in the corresponding URF's. All isomeric dibenzotropones **16**—**19** are also known, among which **18** and **19** have been isolated.[16] Both **16** and **17** are rather unstable and neither has been isolated, apparently because their structures have an *o*-quinonoid form.



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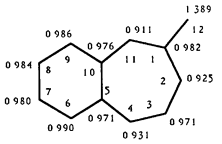

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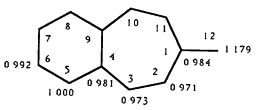

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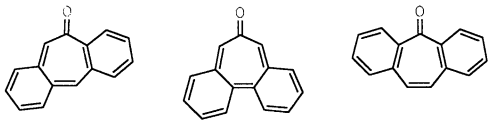
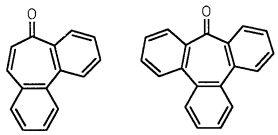


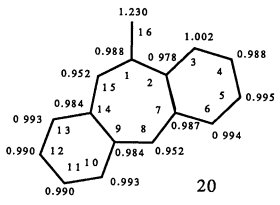
16 17 18



19 24

All *exo*-methylene carbons in the URF's (**20**—**23**) show the largest values of the charge densities in comparison with their ring carbons.

In each case the oxygen atom is located at the *exo*-methylene carbon of the maximum charge density in the URF's **20**—**23**. Tribenzotropone **24** has been



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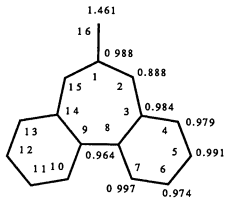

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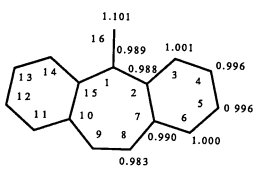

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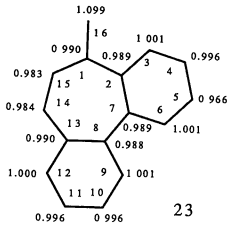

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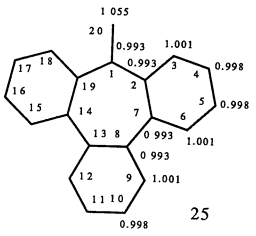
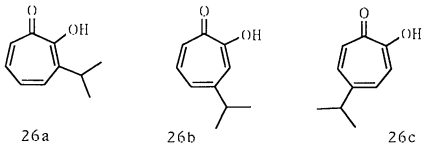


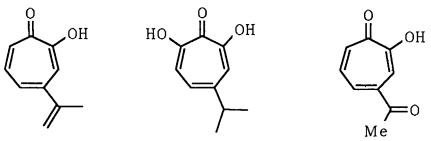
25

prepared.[17] The charge density of the corresponding URF (**25**) reveals that the oxygen atom occupies the site of the largest charge density in the corresponding URF. As metioned above, the fundamental skeleton of the tropones with a unique heptagonal structure is predicted to be aromatic with positive resonance energies and conform to the TCS rule.

Naturally Occurring Troponoids. Various, substituted tropolones such α-, β-, and γ-thujaplicin (**26a**, **26b**, and **26c**, respectively), β-dolabrin (**27**), β-thujaplicinol (**28**), and 4-acetyltropolone (**29**) have been found in the heartwood or essntial oil of various trees of the *cupressales* family, *e.g.* western red cedar.[18] Naturally occurring tropolones have one or more heteroatoms in addition to alkyl substituents. All alkyl substituents are disregarded for simplicity, since they are scarcely conjugated with the parent π electron framework.[4d,e] The URF's for **26a**, **26b**, and **26c** are all identical with that for **4a**. The URF's for **27** and **28** are shown in **30** and **31**, respectively. The oxygen atoms are situated at the sites of large charge density in the corresponding URF's.



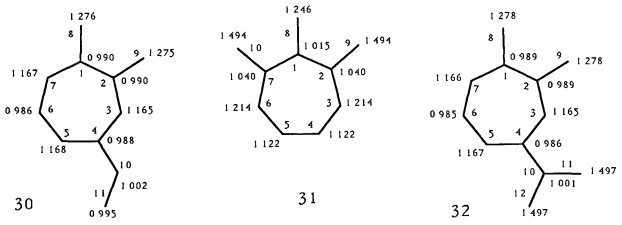
26a 26b 26c



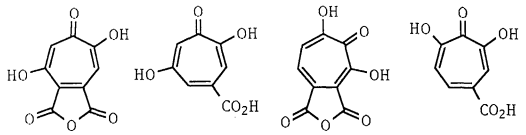
27 28 29

The URF for **29** is the same as that of **30**. The URF for **29** has a high charge density at positions 8 and 9. The two oxygen atoms are placed at the corresponding positions. However, the position of acetyl oxygen does not conform to the TCS rule. The charge density is not high at the corresponding position in the URF. Therefore, we consider that the methyl group is conjugated with the π-electron subsystem of the acetyl group. The charge densities in the URF is shown in **32** (14 π-electrons).

The corresponding URF (**32**) has a large charge density at positions 8, 9, 11, and 12. The correspond-



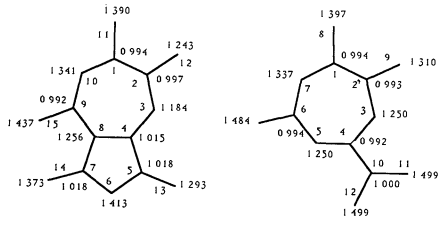
30 31 32



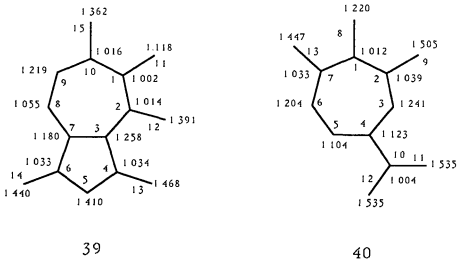
33 34 35 36

ing positions in **29** are all occupied by electronegative heteroatoms and iso-π-electronic substituents. A wide variety of tropolone derivatives have also been found in nature as secondary vegetable metabolites. They include stipitatonic (**33**), stipitatic (**34**), puberulonic (**35**), and puberulic (**36**) acid.[19–22] The URF's for **33**—**36** are shown in **37**—**40**, respectively. The URF's **37**—**40** have large charge densities at just those positions where ketone oxygens and alcohol (or ether) oxygens occur in the natural products.

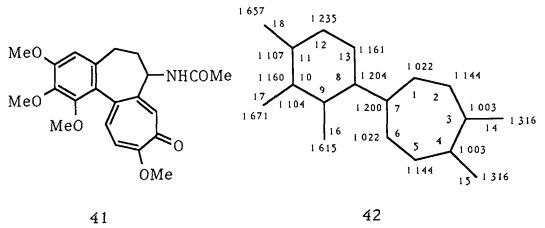
Alkaloidal tropolone derivatives, notably colchicine (**41**)[23] have been found in plants of the *liliacae* species.



37 38

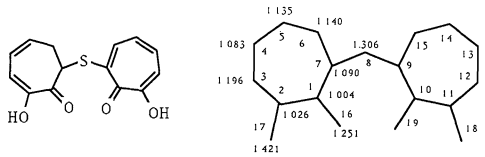


39 40

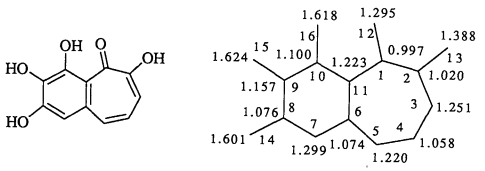


41 42

The colchicine molecule contains four methoxyl groups that are conjugated with the π-electron system. The URF of **41** (**42**) has a high charge density at positions 14—18. Thus, the methoxyl and ketone oxygens are situated at the sites of large charge density in the corresponding URF. The thiobis (tropolone) (**43**) has been isolated[24] from a bacterial culture and shows antibiotic properties. The red coloring matter, purpurogallin (**45**), also occurring naturally in various galls, is a benzotropolone derivative.[25,26] The URF's for **43** and **45** are shown in **44** and **46**, respectively. All positions of high charge density in the URF's are occupied by heteroatoms in the corresponding natural products.



43 44



45 46

In naturally occurring tropolones nature puts oxygens and/or thioether sulfur at the sites of large charge density in its URF. We have also shown that naturally occurring tropolones nicely fit the theory that the conformity to the TCS rule gives a stable molecular system. Molecules that do not conform to the TCS rule can in principle, be designed using an infinite number of molecules; as a natural consequence, many of the troponoids so far synthesized were chosen from energetically very stable molecules and synthetically very accessible molecules.

Annulated Troponoids and Formation Mechanism. After Nozoe and his co-worker's earier study[27] of quinoxalotropone (**47**), Itô and his co-workers[28] obtained **47** and its isomer **48** by the reaction of *p*-and *o*-tropoquinone (**49** and **50**) with *o*-phenylenediamine (**51a**). Asao[29] obtained the tricyclic ditropone **52** from 2,5-diaminotroponeimine (**53**) and 5-nitrosotropolone (**54**). More recently, Takeshita et al.[30] synthesized the pentacyclic ditropone **56** and the tetracyclic tropone **57** from **49** and benzenetetramine. The URF's for two quinones, **49** and **50**, are shown in **58** and **59**, respectively. Three ketone oxygen atoms in these quinone are situated at the sites of large charge densities in the corresponding URF's. The charge densities of the URF's for two quinoxalotropones, **47**and **48**, reveal that the heteroatoms in each isomer

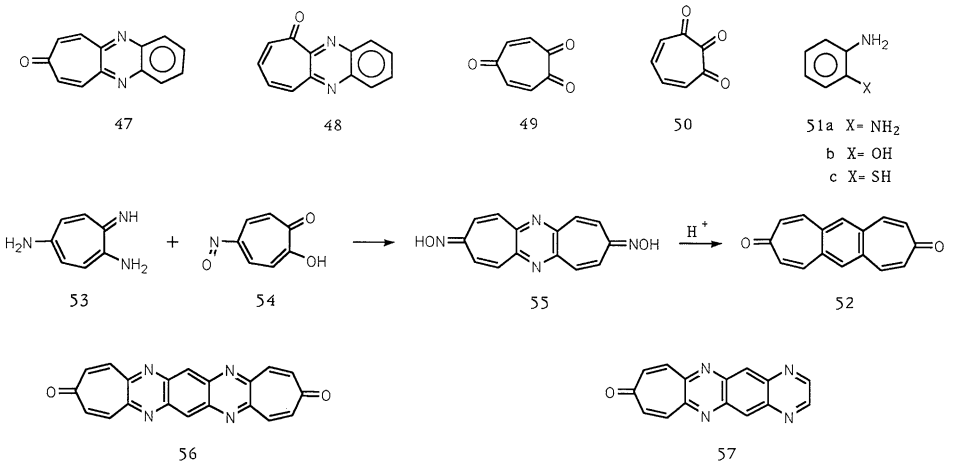
occupy the sites of high charge density in the corresponding URF's (**61** and **62**, respectively). The URF's for two starting materials **53** and **54**, intermediate **55**, and product **52** are shown in **63**—**66**, respectively. The URF's of **63**—**66** have large charge densities at just those positions where heteroatoms occur in these URF's. The values of the resonance energies for the heterocycle-fused troponoids are given in Table 3. In all cases, these compounds can be regarded as being aromatics with positive resonance energies.

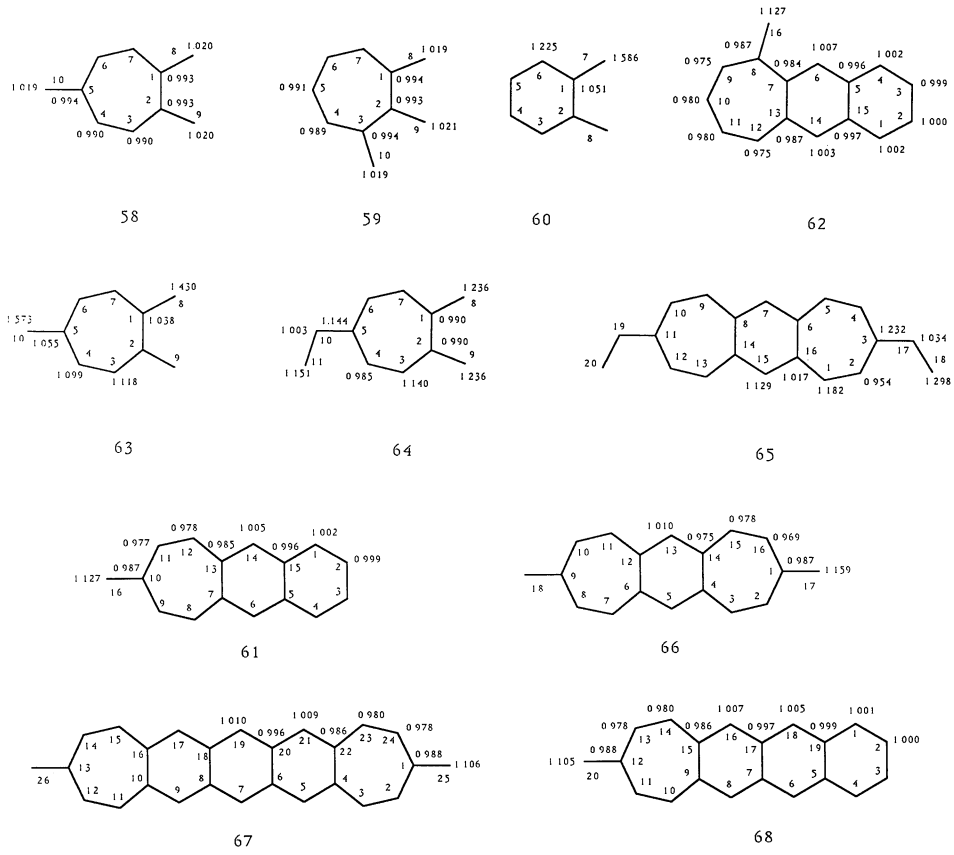
Table 3. Resonance Energies of **47**, **52**, **56**, and **57**

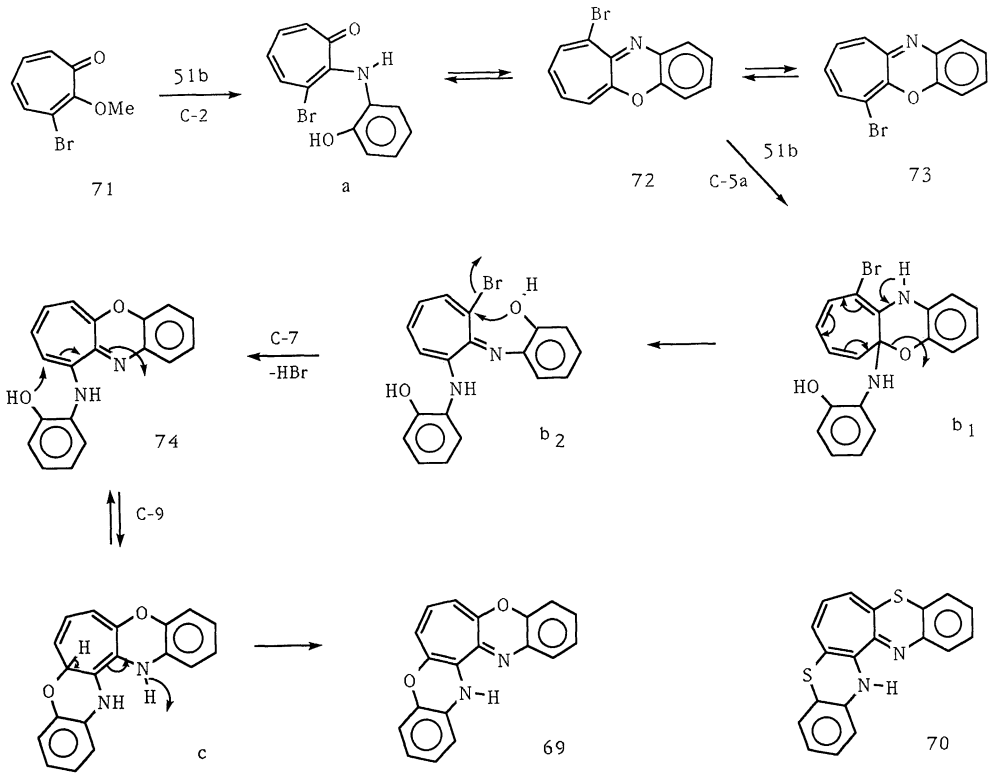
	RE	REPE
47	0.3919	0.0245
52	0.1075	0.0054
56	0.4213	0.0050
57	0.3557	0.0162

RE: Resonance energy (in β unit). REPE: Resonance energy per π-electron.

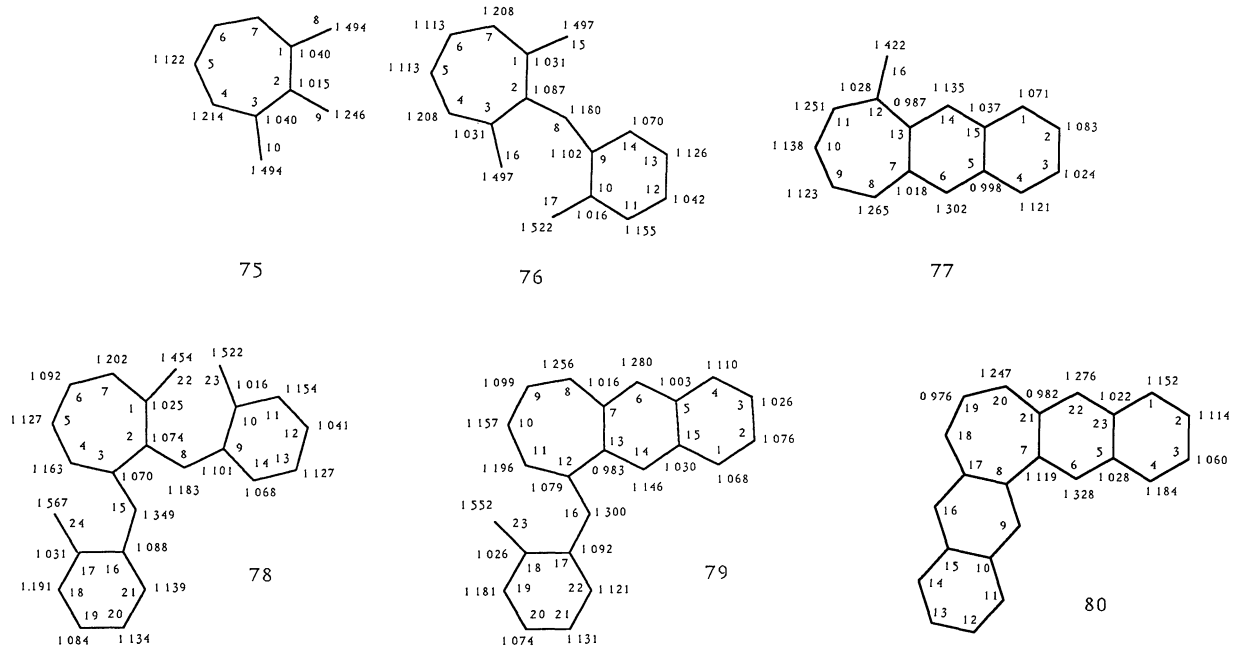
Nozoe and his co-workers recently synthesized 14*H*-dibenzo[1,2-*e*:1′,2′-*e*′]cyclohepta[1,2-*b*:4,3-*b*′]di[1,4]oxazine (**69**) and its *S*-analogues **70**.[31] The possible pathways proposed for the formation of **69** are shown in Scheme 1.[31] The most favorable first intermediate







Scheme 1.

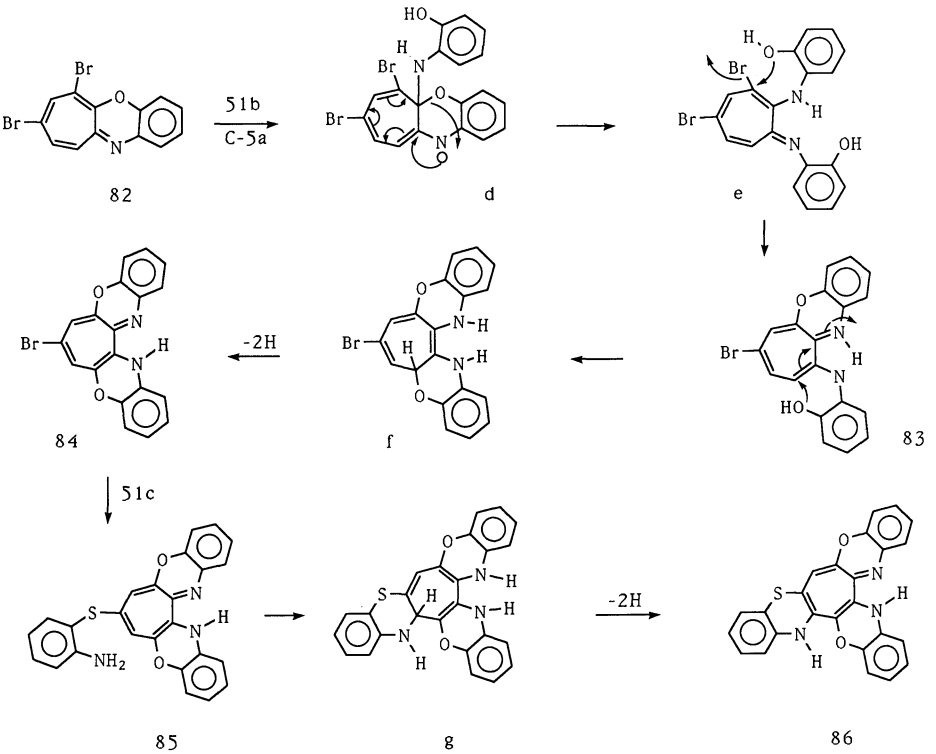


of the reaction of **71** with **51b** was considered to be the 2-substituted intermediate **a**, which then cyclizes to give **72**. We assumed that the amino group of **51b** then first attacks C-5a of **72**, followed by the ring opening shown in $\mathbf{b}_1$ and then bromine substitution ($\mathbf{b}_2$) to give **74**. This compound would readily be transformed to **69** by ring closure at C-9 (**c**) and then dehydrogenation.

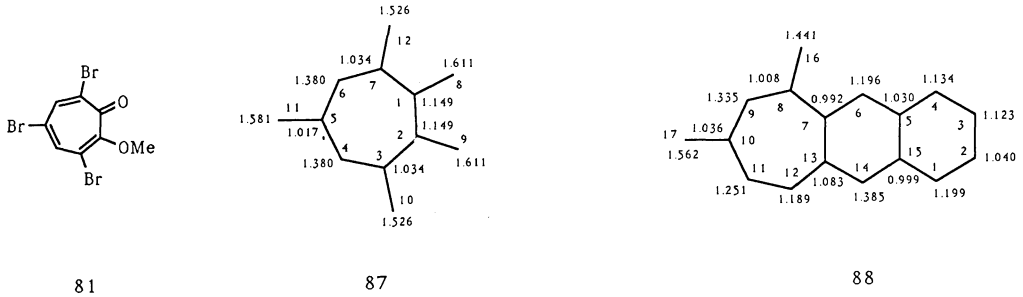
In order to prove the validity of these presumed pathways, Gimarc's TCS rule is applied to the reaction mechanism. The URF's for two starting materials, **71** and **51b**, and intermediate **a** are shown in **75** (12π-electrons), **60**, and **76** (20π-electrons), respectively. The corresponding positions in **71** and **a** are all occupied by electronegative heteroatoms. The URF's for **72** and

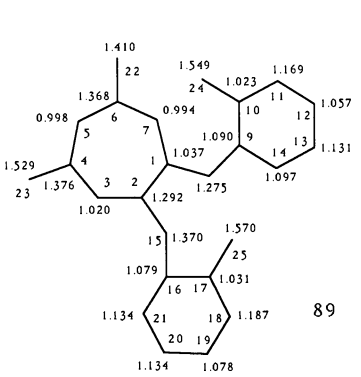
73 are identical with that of **77**. The URF's for intermediate $\mathbf{b_2}$ and **74** are shown in **78** and **79**, respectively. A URF for oxazine **69** and its *S*-analogue **70** is shown in **80**. All positions of high charge densities in the URF's are occupied by heteroatoms in the corresponding molecules. Therefore, the present reaction mechanism can be said to be reasonable in view of the TCS rule.

More recently, Nozoe and his coworkers[6] reported that tropylium compounds having tri-annulated heterocycles **86** are obtained by the reaction of 2,4-dibromo-7-methoxy- and 3,5,7-tribromo-2-methoxytropone (**81**) with *o*-aminophenol (**51b**) and *o*-aminobenzenethiol (**51c**). They also discussed possible pathways for these reactions (Scheme 2);[6] theoretical calculations by means of a semiempirical molecular orbital method, such as MNDO, encountered difficulties in predicting the formation mechanism of such large conjugated systems. 7-Bromo-14*H*-cyclohepta[1,2-*b*:4,3-*b'*]bis-[1,4]benzoxazine (**84**) was prepared form the 6,8-dibromo compound **82** and **51b** by an intramolecular, hetero-ring transposition via **d**, **e**, **83**, and **f**, followed by dehydrogenation. The URF's for two starting materials, **51** and **81**, are shown in **60** and **87**, respectively. Heteroatoms and iso-π-electronic substituents in these molecules are situated at the sites of large charge density in these respective URF's. The URF of **e** has large charge densities at positions 7, 15, 22, and 23. The corresponding positions in **e** are all occupied by electronegative heteroatoms. The URF's for **83** and intermediate **f** are shown in **90** and **91**, respectively. The URF's **90** and **91** have large densities at just those positions where heteroatoms occur in **83** and intermediate **f**. The URF of benzoxazine **84** (**92**, 28 π-electrons) has high charge densities at positions 6, 8, 10, 12, 19, 22, and 24. Though positions 8 and 10 in the URF of **84** have high charge densities, the corresponding positions have no heteroatoms there. According to the original TCS rule, it is not necessary to place heteroatoms at all of the sites of high charge



Scheme 2.

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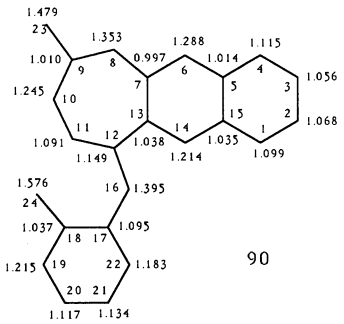
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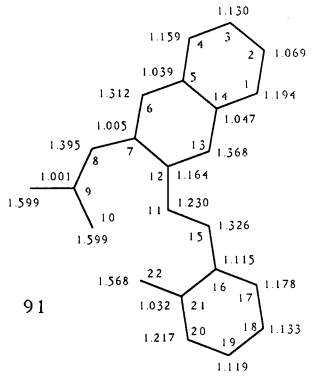
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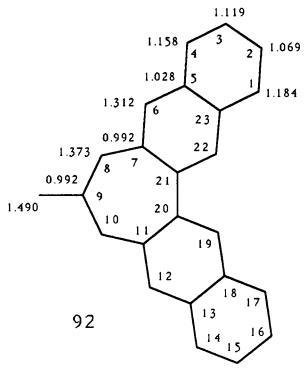
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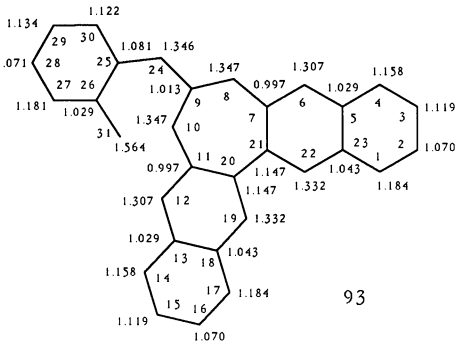
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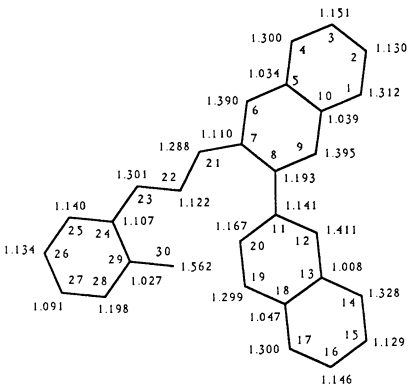
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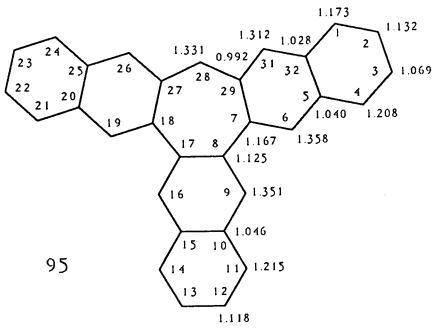
95

density in the URF to stabilize molecules. Five heteroatoms are sufficient to stablize the benzoxazine-conjugated system **84**. As shown in Scheme 2, when **84** and **51c** were allowed to stand at room temperature *S*-substituted compound **85** was obtained. Compound **85** was dehydrocyclized to give **86**. The URF's for **85**, intermediate **g**, and tri-annulated heterocycle **86** are shown in **93**, **94**, and **95**, respectively.

The heteroatoms in these compounds are situated at the sites of large charge density in their respective URF's.

As shown above, the starting materials, intermediates, and several products in these reactions are fully consistent with the TCS rule. The presented reaction mechanism appears to be in conformity to the process energetically in the direction of the most favorable route.

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