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NONBENZENOID PHANES

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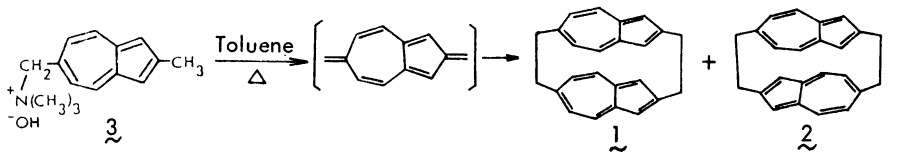
Abstract— Phanes containing so-called nonbenzenoid aromatic rings such as azulene, tropolone, p-tropoquinone and tropone are discussed with emphasis on their conformations and transannular interactions. Some of their chemical reactions are also discussed.

INTRODUCTION

Chemistry of cyclophanes initiated by ingenious studies of Cram and others has been quite prosperous for 30 years and made a large contribution to the entire field of aromatic chemistry. This is reminiscent to the even greater contribution of the studies of nonbenzenoid aromatic compounds to the same field. Therefore it was quite natural for a man grown up in the field of nonbenzenoid aromatic chemistry to dream the combination of these two general fields and try to investigate phane systems with nonbenzenoid rings. This seemed especially worthwhile from the following considerations. The delocalization energy per electron of nonbenzenoid rings is in general considerably smaller than that of benzenoids, and therefore when incorporated in phane systems with short bridge(s), the former rings may be deformed to a larger extent than the latter in order to release the internal strain. In a double-decked phane these rings may exhibit stronger transannular interaction than benzenoid because they are often associated with a charge (as in tropylium ion) or dipoler structure (as in tropone and azulene). Finally these modifications in structure and physical properties may cause a large change in the reactivity of parent ring systems so that interesting chemistry can be expected. With these anticipations, we have carried out investigation of the phanes containing azulene, tropone or tropolone rings. The present lecture provides with our result with the emphasis on their geometries, transannular interactions, and some of their chemical reactions.

[2.2](2,6)AZULENOPHANES

The first azulenophanes synthesized are syn- and anti-[2.2](2,6)azulenophanes (1 and 2). They were obtained as a 5:4 mixture in 1976 by two groups (1). The final step in the syntheses was Hofmann-type degradation, one of the general methods for the synthesis of phanes, of the quaternary ammonium salt 3 of 6-dimethylaminomethyl-2-methylazulene. The yield of the coupling of the transient quinodimethane was 56%.



3 1 2

The mixture was separated by careful chromatography at -30°C on SiO_2 impregnated with phosphoric acid to give 1 and 2, both dark greenish blue prisms decomposing over 300°, in 55% and 41% yield, respectively (2). Their structures were assigned unambiguously from their PMR spectra: The methylene proton signals appear as complex AA'BB' for 2, while those of 1 are two clear singlets.

Geometries

The crystals of 1 and 2 are completely disordered, precluding determination of their precise geometries. However, our preliminary result of X ray analysis indicates that both molecules are in a barrel shape. This is also indicated by the chemical shifts of their azulenic protons (Table 1). Although all protons in 1 and 2 show up-field shifts (+values) compared with those of 2,6-dimethylazulene 4, their shift values are smaller for H_4 than for H_1 and H_5 and the values for the latter two are comparable. These facts suggest a longer interplaner distance in the central part than in the tip part.

TABLE 1. Comparison of PMR chemical shifts (δ) of 1, 2 and 4

Compds	1		2		4
Δδ		4 - 1		4 - 2	
$H_{1(3)}$*	6.47	+0.67	6.43	+0.71	7.14
$H_{4(8)}$	7.65	+0.42	7.60	+0.47	8.07
$H_{5(7)}$	6.37	+0.71	6.40	+0.68	7.07

*azulene numbering

Transannular interaction

The electronic spectra (Figs. 1 and 2) of 1 and 2 in neutral solvent are very similar to each other, and when compared with that of 2,6-dimethylazulene 4, not much difference is observed except disappearance of fine structures and some bathochromic shift, both common features in [2.2]-phanes (3). The similarity in electronic excitation between 1 and 2 was also indicated by their photoelectron spectra obtained by Heilbronner (4). These similarities may be taken as more evidences that azulene itself is best represented by the perturbed [10]annulene structure. The small transannular interaction can be explained by the inefficient interaction of the HOMO of an azulene ring with the LUMO of another azulene both in syn- and anti-orientations.

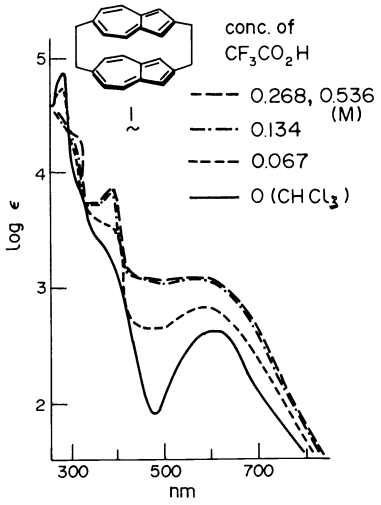


Fig. 1. Electronic spectra of 1 in neutral and weakly acidic media.

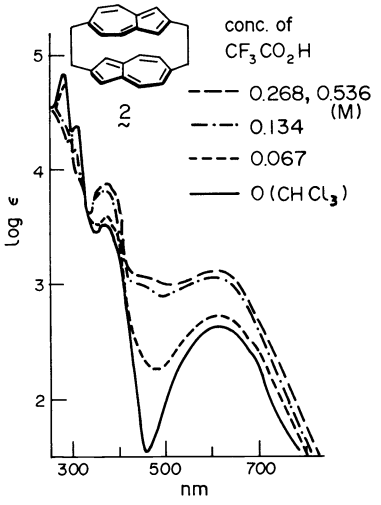


Fig. 2. Electronic spectra of 2 in neutral and weakly acidic media.

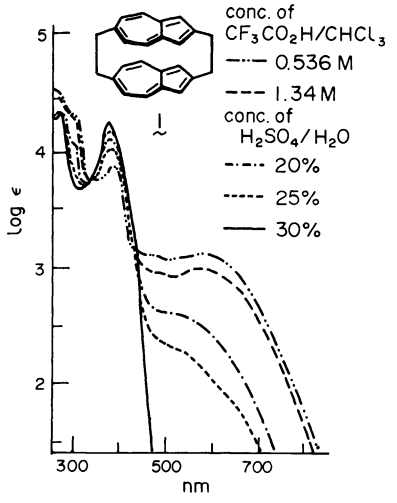


Fig. 3. Electronic spectra of 1 in stronger acid.

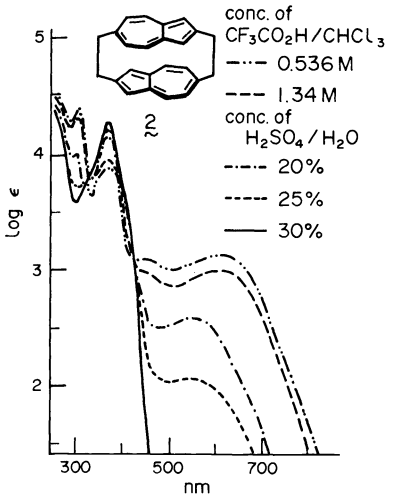
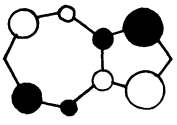
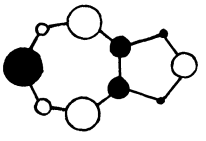


Fig. 4. Electronic spectra of 2 in stronger acid.

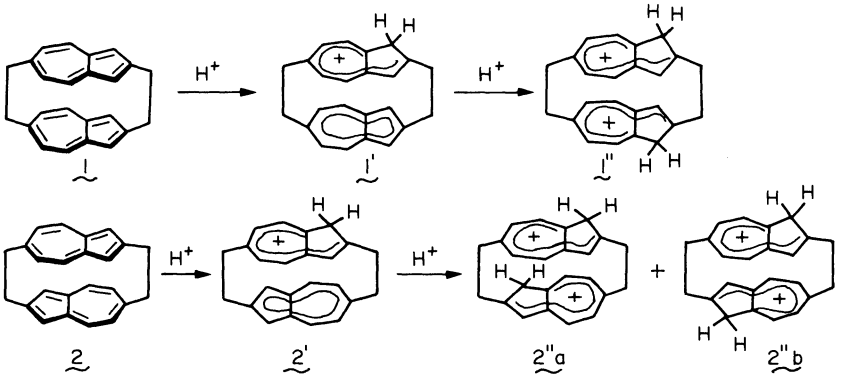


HOMO (φ_5)



LUMO (φ_6)

Electronic spectra in acidic media shows much stronger transannular interaction in monoprotonated species (Figs. 1-4). The new absorption band appears at ~470 nm on addition of trifluoroacetic acid, reaches a maximum at 0.2~0.5 M concentration in both cases, and fades away on further addition of acid to culminate in the spectra identical with that of 4 under the same conditions. These changes should be associated with the mono- and diprotonation processes, 1 → 1' → 1" and 2 → 2' → 2". PMR spectra in strong acid disclosed that 1" contained only one species implying strong preference in the site of second protonation of 1', while 2" was a 3:1 mixture of two species, 2"a and 2"b. The structure with C_2 symmetry is proposed for 1" for the steric reason. Since azulenium ion is known to be transparent in 470 nm region, the newly-formed bands should be due to the CT interaction and their close similarity both in position and intensity clearly indicates the similarity in 1' and 2' in the interaction and therefore stabilization.



However, a closer examination of basicity revealed the following facts; 1) both 1 and 2 are stronger bases than 4, 2) 1 is slightly stronger base than 2, 3) 1' and 2' are weaker bases than 4 and 4) 1' is slightly weaker than 2'. The situation can be depicted schematically as in Fig. 5 in the energy term; energy difference between 1 and 2, and 1" and 2" are larger than that between 1' and 2', where CT interaction occurs almost equally. While instability of 1" compared with 2" is easily understood as the result of more serious Coulombic repulsion, 2 owes its comparative stability, we believe, to a small but significant contribution of the dipolar structure of azulene.

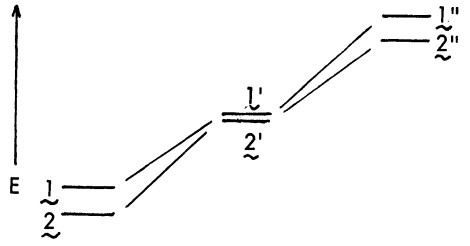


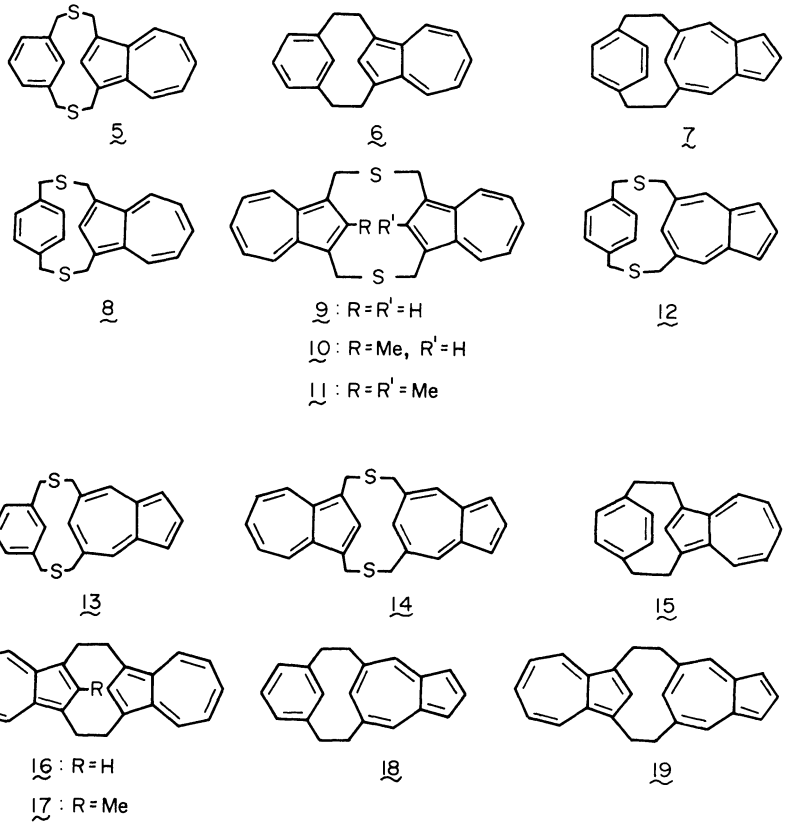
Fig. 5. Energy diagram of protonation of 1 and 2.

1,3- AND 5,7-BRIDGED AZULENOPHANES

Investigation was extended to azulenocyclophanes and azulenophanes with the bridges at 1 and 3 positions or 5 and 7 positions of azulene ring. Three azulenocyclophanes 5 - 7 of this type had already been synthesized, the first two by Murata (5) and the last one by Misumi (6). We included these compounds in our comparative study.

Synthesis

Employing the photochemical sulfur extrusion method, one of the general routes to cyclophanes, the azulenophanes 5 - 19 were synthesized from 1,3- and 5,7-bis(trimethylammonium methyl)azulenes (7).



Geometries of [2]azuleno[2]cyclophanes and [2.2]azulenophanes

X-ray analysis of 15 and 16 discloses that both azulene and benzene rings have rather normal bond lengths and bond angles in both compounds, but both rings show vertical deformation at the bridging site. Their precise conformations in crystals are shown in Fig. 6.

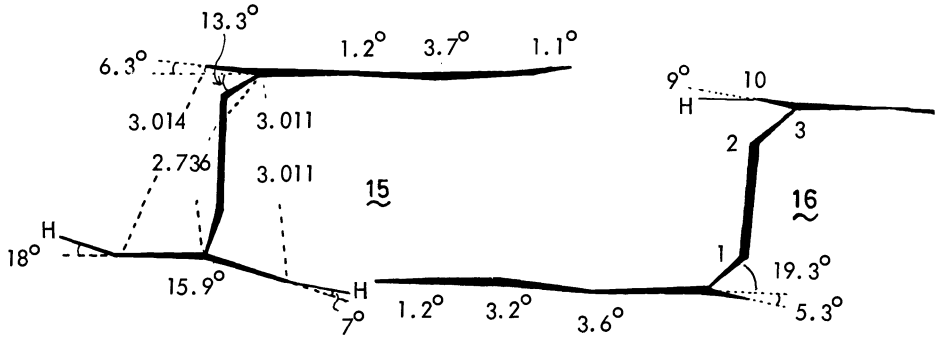
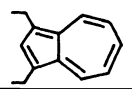
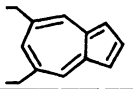
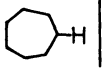


Fig. 6. Side views of 15 and 16 with some interatomic distances.

The anti geometries and their rigidity in solution were suggested from PMR spectra of all compounds examined. The chemical shifts of aromatic protons show large up-field shifts for the inner protons and small shifts (both up-field and down-field) for the outer protons when compared with the corresponding chemical shifts of the reference compounds 1,3- and 5,7-dimethylazulenes (20 and 21), and m- and p-xylenes. When classified by the size of the rings which are directly facing the protons and on which the proton is attached, some regularity emerges as shown in Table 2 in the shift values in the meta-bridged phane series: Although being dependent to some extent on the size of ring where the proton is attached, the shift values fall in small ranges depending on the size of the facing ring and, on going from 5 membered ring to 7, a clear decreasing order can be observed. The same is true for the values (in the parentheses in Table 2) for inner protons on para-bridged benzene rings though to a lesser extent.

TABLE 2. Shift values of the inner protons of some phanes

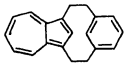
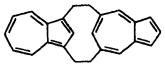
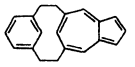
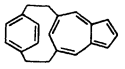
			
	+3.09	+2.34	+1.70
	+3.75 (+1.92)	+2.62*1 (+1.24)*2	+1.75 (+1.16)
	+4.07	+2.46	—

*1 reference 8, *2 reference 9

Since an up-field shift we are discussing depends on the relative position of a proton to the facing ring, the observed up-field shift may be utilized to define at least time-averaged geometry of the phanes in solution. Thus we attempted to estimate the position using the line current approach (10). The line current values of benzene and azulene rings are first modified respectively to those for symmetrical [2.2]metacyclophane 22 and 16, whose geometries are known by X-ray analysis (11). The values evaluated for benzene ring was checked with [2.2]paracyclophane 24 taking the geometry defined by X ray analysis (12). The calculated up-field shift value (+0.61 ppm) agrees well with the observed one (+0.60 ppm) (13). The evaluated value for azulene ring was applied to the asymmetrical 15, again using conformation defined by X ray analysis (interplaner angle 9°) to yield the shift values for all protons. However, the best-fit values were obtained when azulene ring was adjusted to be parallel to the mean plane of benzene ring. The values thus obtained are H_2, +1.45; H_4, +0.19; H_5, -0.03; H_6, -0.06; H_i, +1.97; H_o, +0.05; to be compared with the observed ones, +1.40, +0.14, -0.36, +0.06, +1.92, +0.12 (in the same order). Despite of the very coarse approximation, the calculated shift values are in good agreement with the observed ones.

Since the method was successfully used to define the interplaner angle, we extended calculation to other asymmetrical molecules. The shift values and the interplaner angles for four compounds are listed in Table 3.

TABLE 3. Observed and calculated up-field shifts (ppm) of inner protons and interplaner angles (θ)

Compounds	rings	up-field shifts obs.	up-field shifts calcd.	θ
 6	azul.	2.34	2.45	13°
	bz.	3.75	3.75	
 19	1,3-bridged	1.70	1.84	16°
	5,7-bridged	4.07	4.07	
 18	azul.	2.46	2.46	1°
	bz.	1.75	2.04	
 7	azul.	1.48	1.59	23°
	bz.	1.16	1.03	

The estimation of the energy barrier for the ring flipping was next attempted for 15, but PMR spectrum showed no indication of such a process up to 190°C, from which the energy barrier was estimated to be at least 22.0 kcal/mol (assuming $\Delta\delta$=180 Hz). This value compares with those of 23 (20.6 kcal/mol, Tc=146°C) (14) and 7 (estimated to be 16.2 kcal/mol, Tc 70°C) (6). The differences may be resulted from the stability of the rotational transition states. In the transition states, the steric repulsion between the inner hydrogen and the facing para-bridged benzene ring would be increased in the order of 7-, 6- and 5-membered rings. The distances of the hydrogen and the benzene calculated from the X ray data are ~1.2 Å for 15, ~1.5 Å for 23 and ~1.75 Å for 7.

Charge transfer interaction

Electronic spectra (Fig. 7) of azulenophanes 16 and 19 exhibit, as in those of 1 and 2, the loss of fine structure, broadening and small bathochromic shift in all absorption bands. Although a small shoulder is observed at ~400-500 nm the absence of a clear CT band shows inefficient HOMO-LUMO interactions in these compounds.

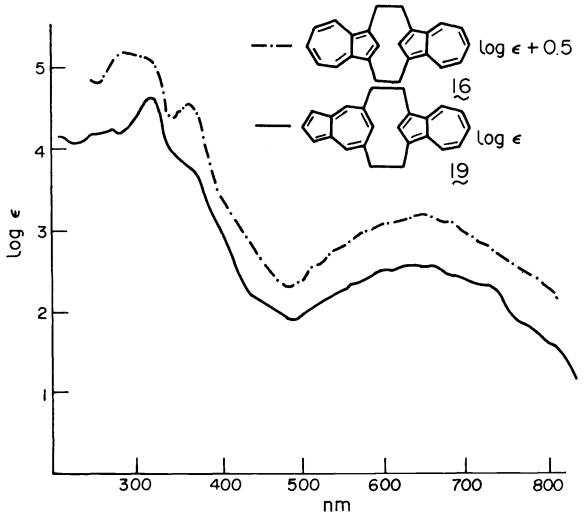


Fig. 7. Electronic spectra of 16 and 19.

Spectra of azulenocyclophanes, 6, 7, 15 and 18, shown in Figs. 8 and 9, also show same features as in 16 and 19.

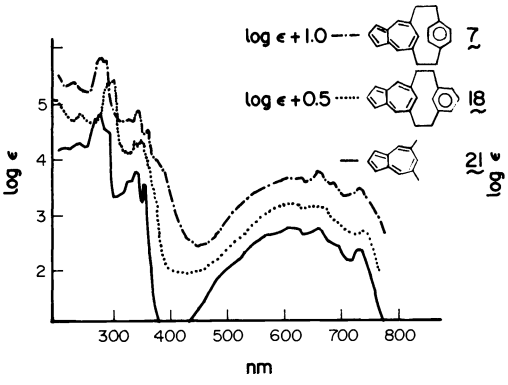


Fig. 8. Electronic spectra of 7, 18 and 21.

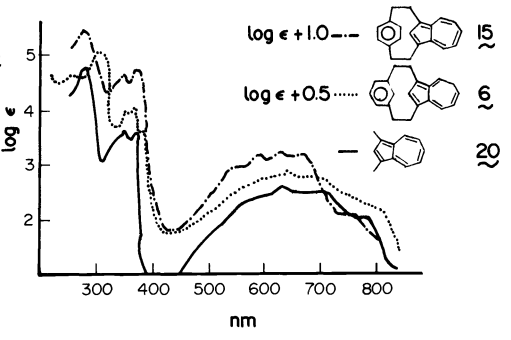


Fig. 9. Electronic spectra of 6, 15 and 20.

Another feature noted is the large bathochromic shifts (~2760 cm^{-1}) of ^1Bb bands in metacyclophanes 6 and 18 compared with the para counterparts 7 and 15. The result of extended Hückel MO calculations for 7 and 18 (Fig. 10) explains the difference.

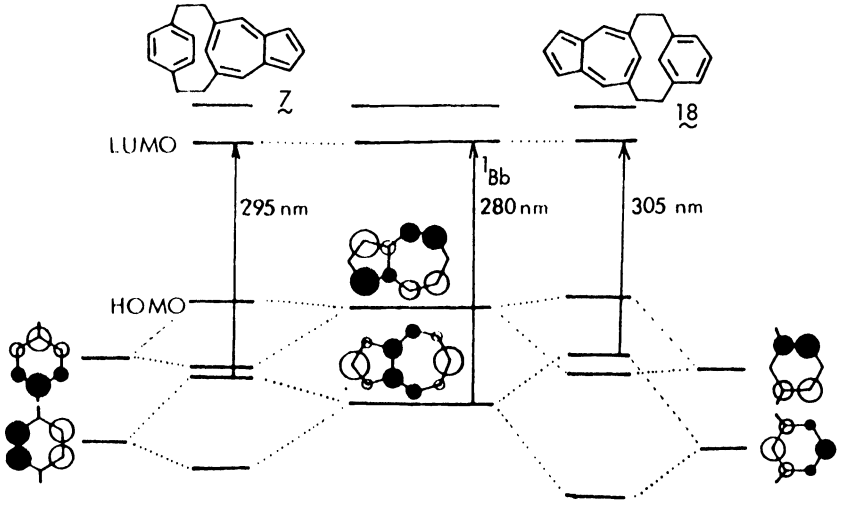
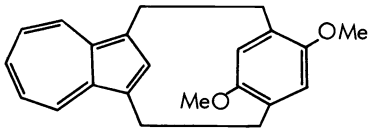
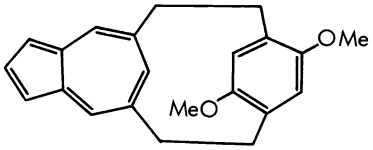


Fig. 10. Schematic diagram of orbital interaction in 7 and 18.

The ^1Bb absorption (280 nm) of azulene is known to originate from the excitation from next HOMO. Since all of the azulenocyclophanes under consideration belongs to C_s point group, symmetrical orbitals of azulene and benzene can interact in principle. However, the geometry of 7 does not allow as much efficient mixing of the orbitals as in 18 where strong mixing is expected. Thus the two composed symmetrical orbitals in 18 split more than those in 7, and the excitations therefrom shift the ^1Bb absorption to the longer wave lengths for 18 than for 7. When two methoxyl groups are introduced in benzene rings, however, appearance of a shoulder (ca 400 nm) and bathochromic shift of ^1Bb band were observed even in the paracyclophanes 25 and 26, implying better interactions of orbitals.



25



26

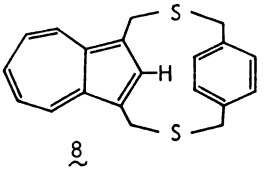
In contrast to neutral species described, protonated cation of these compounds shows clear CT bands at 400-500 nm, corresponding to 420-500 nm in 1' and 2'. It is interesting that even 5,7-dimethylazulene 21 shows such a band (~420 nm) of weak intensity at 0.1% trifluoroacetic acid in CH_2Cl_2. This is probably due to the stacking between a protonated and nonprotonated molecules. Another general feature is the retention of the ^{1}Lb bands in all cases suggesting weaker basicity of azulene rings than the corresponding dimethylazulenes. In the azulenophane 19, the CT state causes a large bathochromic shift of ^{1}Lb band extending nearly 1000 nm. The azulenometacyclophane 6 undergoes rapid reaction in acid, which will be discussed later.

Conformation of dithia[3.3]azulenophanes and -azulenocyclophanes

PMR spectra of all of these compounds with no extra substituent reveal the presence of dynamic processes at room temperature, showing one or two sharp singlets due to methylene protons. This is in accord with the behavior of [3.3]metacyclophane (16) and its dithia analog (17). In order to establish the conformational preference and the activation energy for the dynamic process, their PMR was examined at low temperatures. Conformational flexibility in these compounds originates from the flipping of azulene rings and the conformational changes in S-containing bridges, but it turned out that the former process has higher activation energy than the latter in general.

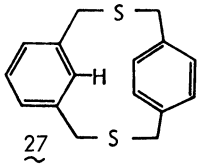
Paracyclophanes 8 and 12. PMR spectrum of (1,3)azulenophane 8 starts broadening at -110° and the signal due to benzene protons coalesces at -125° and becomes doublet at -135°. From these data, the activation energy was calculated to be $\Delta G^{\ddagger}$=7.0 kcal/mol. Since all signals especially those due to bridge protons still shows broadening at -135° process frozen is the ring flipping and the conformational change of the bridge is still operating even at this temperature. On the other hand, PMR spectrum of the corresponding (5,7)azulenophane 12 shows no sign of broadening at -110°, so that, although $\Delta G^{\ddagger}$ value was not obtained, the activation energy for the ring flipping should be less than 7 kcal/mol. The larger activation energy in (1,3)azulenophane than the (5,7)-counterpart is in accord with the result in [2]azuleno[2]paracyclophanes 7 and 15.

The up-field shift values of the inner protons of 8 and 12 compared with the respective reference compounds are shown below together with that of 27 (18) and indicate the difference in the time-averaged relative position of the hydrogen to the facing benzene rings; on going 12 → 27 → 8, the inner hydrogen seems shifted off the center of shielding cone of benzene rings.



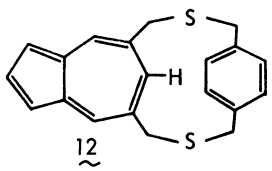
8

Δδ +1.17



27

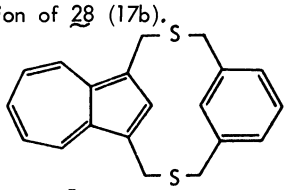
+1.36



12

+1.61

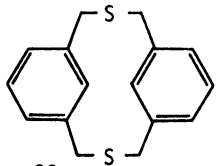
Metacyclophanes 5 and 13. The shift values of the inner protons in 5 (5), 13 and 28 (19) shown below are much smaller than those of 8, 12 and 27. The predominant contribution of syn conformation at room temperature was suggested for 5 and 13 from these observations and the known preferred syn conformation of 28 (17b).



5

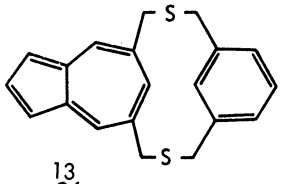
azul. bz.

Δδ -0.12 +0.32



28

+0.11



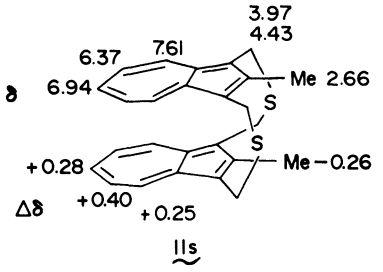
13

azul. bz.

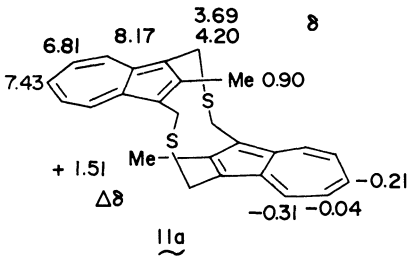
+0.63 -0.07

This was verified by the low-temperature PMR measurement; all aromatic protons of 13 appear at -100° as a pair of signals with the 3:2 intensity ratio. Since there is no aromatic proton in the higher field, the compound is frozen in two syn forms. The activation energy for the ring flipping was estimated to be ~10.5 kcal/mol using coalescence method. For 5, coalescence temperature was difficult to estimate because of the extensive overlap. Activation energy estimated from one of the bridge proton signals is ~10 kcal/mol.

Azulenophanes 9, 10, 11 and 14. PMR spectrum of dimethylazulenophane 11 at room temperature clearly shows two sets of signals for all protons including AB type of methylene protons, indicating the presence of two rigid conformations. From the chemical shifts and intensities, these signals can be assigned to the syn and anti conformers, 11s and 11a, as indicated below along with the shift values (Δδ) from 1,2,3-trimethylazulene 29. It is clear from the shift values that even in dithia[3.3]phanes the anisotropic effect of azulene ring is quite significant.

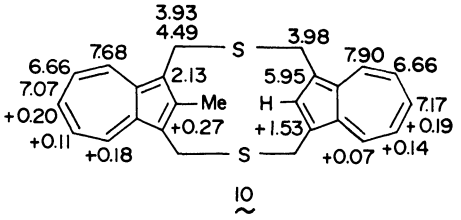


11s

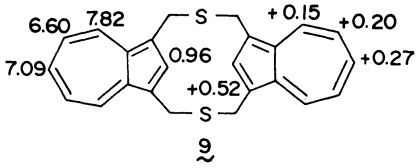


11a

The methylene signals in the spectrum of monomethylazulenophane 10 consist of a 4H singlet and a 4H AB quartet, implying that, while 2-methylazulene ring is frozen, the other azulene ring is freely flipping at room temperature. The signals can be assigned and the Δδ values from 20 or 21 was deduced as shown.



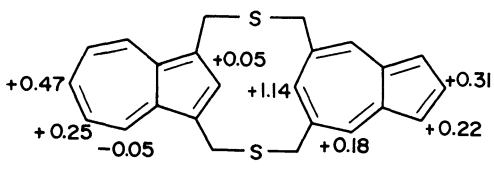
10



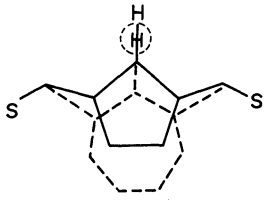
9

In 9, the ring flipping is occurring freely at room temperature. The assigned chemical shifts of ring protons indicate the predominance of syn conformation. At -120°, the inner protons appear as a singlet at ca 5.8 ppm but its intensity is ca 0.3 H. The chemical shift and the intensity reveal that the compound exists at the temperature as a 7:3 mixture of syn and anti conformer. Therefore, syn conformer is ca 0.3 kcal/mol more stable than anti form. The activation energy was estimated to be $\Delta G^{\ddagger}$=9 kcal/mol.

The azulenophane 19 is in the same situation as far as the ring flipping is concerned. Signals can be assigned to all protons by changing temperatures and considering the chemical shifts and coupling constants of azulene. The shift values from the reference compounds, 20 and 21, are shown.



19



Most of the outer protons shows up-field shifts from which the preferred syn conformation can be concluded. However, the shift values of the inner protons are rather puzzling. We believe that these are associated with difference in the time-averaged position of two hydrogens; the one on 5-membered

ring is located off-centered to the shielding cone of the other azulene ring compared with the one on 7-membered ring, because as shown above of the bond angle difference in the rings. Molecular models show the situation clearly (20). Methylene singlets start broadening at -40° and became two AB types at -70°, indicating the freezing of ring flipping. The chemical shifts of aromatic protons suggest the presence of syn conformation only. Thus the potential energy difference of the two conformers should at least be ca 1.5 kcal/mol. The activation energy for the flipping is calculated to be 12 kcal/mol (21).

Energy diagrams for the ring flipping in azulenometacyclophanes 5 and 13 and azulenophanes 9 and 14 (Fig. 11) clearly indicates 1) syn conformations are always more stable than anti forms, and 2) assuming that the potential energy of rotational transition states is equal for all compounds, syn form of 9 is less stable and that of 14 is more stable than those of 5 and 13 which are nearly equal.

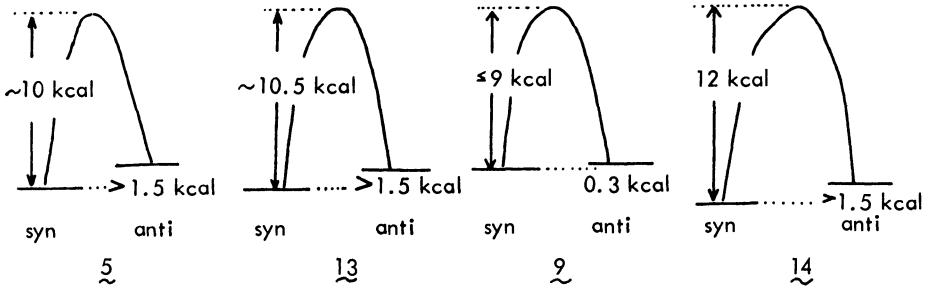
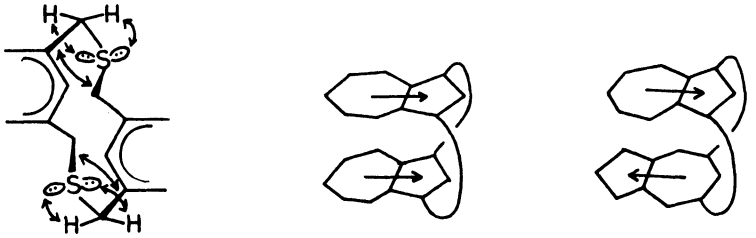


Fig. 11. Energy diagrams of ring flipping in 5, 9, 13 and 14.

The reason for the preferred syn conformation, which is in agreement with [3.3]metacyclophane (16) and its dithia analog 28 (17b) is believed to be steric in nature. As molecular models of any of these compounds show clearly that all atoms attached to the central methylene carbon or the substituent and lone pairs of sulfur (sp^3 assumed) are always in gauche form with both of adjacent methylenes as long as the aromatic rings are held syn, parallel and as distant as possible to each other. In the anti conformation, on the other hand, they are always in eclipsed forms with either one of adjacent methylenes as illustrated below.

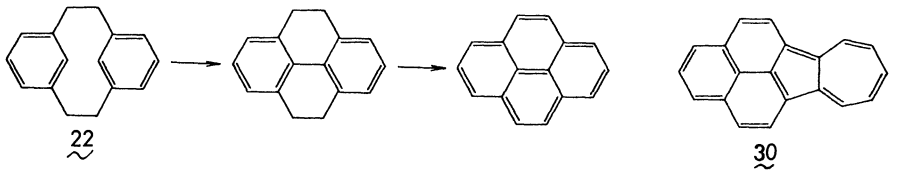
Our rationalization for the second point is the dipole-dipole interaction in the syn forms of 9 and 14 (9s and 14s). Since the bridges are long enough, the rotational transition states in these four compounds are expected to be at nearly equal energy level. The difference in rational activation energy therefore originates from the energy of the syn forms. In the syn forms of 5 and 13, in which benzene is facing to azulene, no interaction is expected. In 9s and 14s, on the other hand, where two dipolar azulenes are facing each other, the dipole-dipole interaction occurs which would destabilize 9s, and stabilize 14s to result in the order 14 > 5 ≃ 13 > 9 of the activation energy. Thus considering the steric repulsion as the major factor and the dipole-dipole interaction as the minor one, the conformations of dithia[3.3]azulenophanes can be explained satisfactorily.



9s 14s

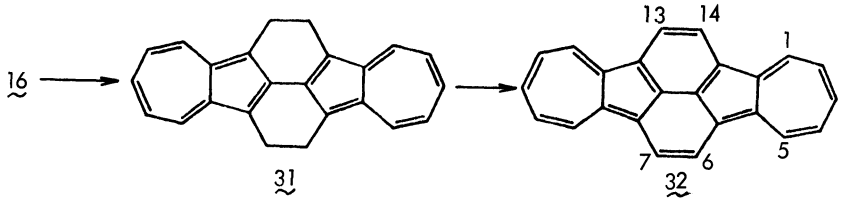
Transannular reactions of [2.2]azulenophanes

One of the unique reactions of [2.2]metacyclophane 22 is its transannular reaction to tetrahydropyrene and the derivation of pyrene therefrom (22). The reaction sequence was applied by Murata to 18 in his synthesis of azulenophenalene 30 (5). If the reaction proceeds with our azulenophanes 16 and 19, it would provide a way to synthesize totally unknown nonalternant isomers of dibenzopyrene. With this expectation, the transannular reactions of 16 and 19 were investigated.



22 30

Although 19 gave no clear product, 16 yielded the corresponding 2,2-biazulene derivatives 31 in 85% yields when treated with iodine in dichloromethane, and chloranil oxidation of 31 gave the desired diazuleno[1,2,3-d,e;1',2',3'-i,j]naphthalene 32 in quantitative yield.



31 32

In agreement with the prediction by Creig rule (23), 32 is aromatic as shown by its PMR spectrum: H_2 and H_3 signals (δ 7.42, 7.92 ppm, respectively) shifted down field by 0.52 and 0.60 ppm, respectively, compared with those of 31, indicating the increase of diamagnetic ring current in the periphery of the molecule. The electronic spectrum of 32 has features common to 30, 31 and tetra-t-butyltetradehydro[22]annulene 33 (24) (Fig. 12), but absorption extends to as long wave length as 1500 nm. Since crystals were not suited for X-ray analysis, we have made some theoretical calculations in order to deduce its main resonance contributor. The semi-empirical SCF-LCAO-π-MO calculation, using variable length method developed by Nakajima (25), always resulted in the structure 32a with the predicted transitions at 340, 521 and 979 nm, starting from any initial structures of C_{2h}, C_{2v}

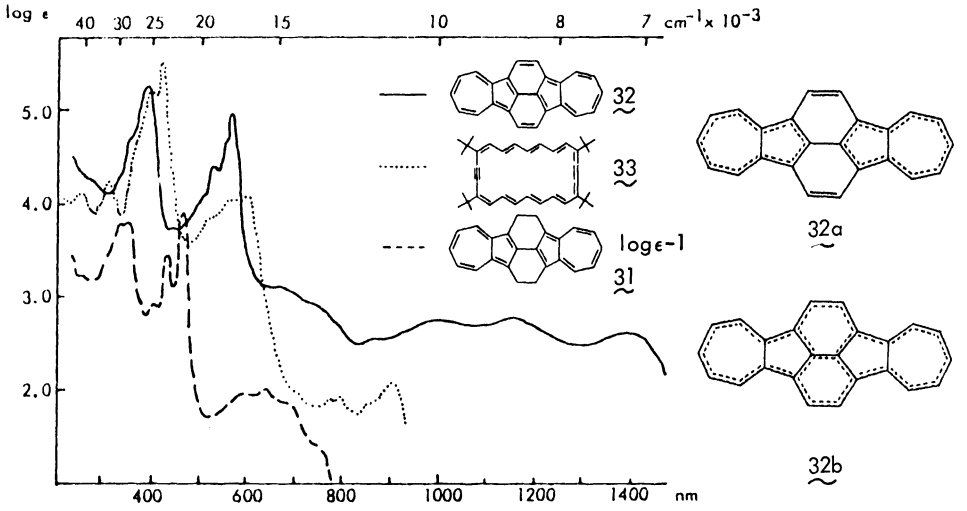
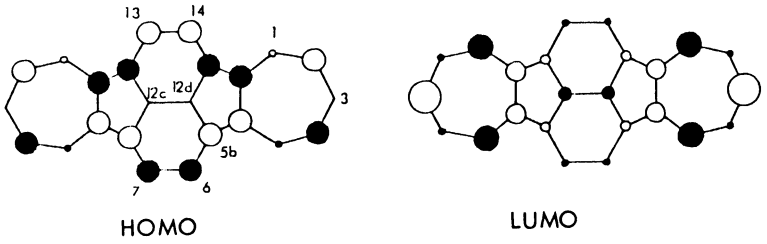


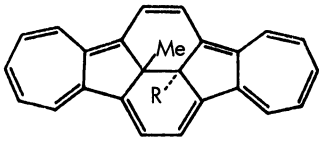
Fig. 12. Electronic spectra of 31, 32 and 33.

(two types) or D_{2h} symmetry. Since the elongation of the bonds C_6-C_7 and C_{13}-C_{14} and the shortening of C_{5b}-C_6 bond and its equivalents would increase the orbital energy of HOMO, but not as much of LUMO of 32 (see the orbital expressions on next page), and therefore result in the bathochromic shift of the absorption in the longest wave length, we next calculated absorptions for the model 32b using PPP-CI method, by which transitions at 346, 563 and 1283 nm, the values closer to the observed ones (383, 553, 1397 nm), were obtained. The structure of 32 may therefore be best represented by 32b.



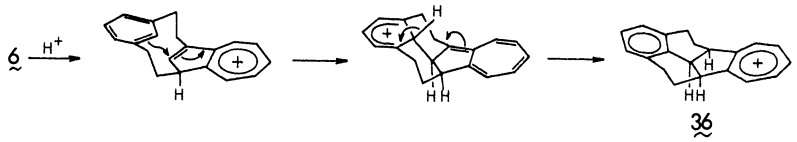
HOMO LUMO

Synthesis of dihydro derivatives 34 and 35, model compounds for peripheral conjugation, were attempted next, following the precedence in pyrene series (19). Thus, methyl and dimethyl azulenophanes, 10 and 11, were subjected to the photochemical desulfurization. The reactions were however very slow and gave complex mixtures. While methylazulenophane 17 was obtained in only 4% yield from the former reaction, small amounts of cleavage products were obtained from the latter. Although further step is being tried with 17, the transannular product 34 has not been isolated up till now.



34 : R=H
35 : R=Me

Another type of transannular reaction was observed during the measurement of electronic spectra of 6 in acidic media. The spectrum changed rapidly to that shown in Fig. 13, and no 6 was recovered on neutralization afterward. PMR spectrum immediately after the addition of CF_3CO_2H showed two inner proton singlets at 5.73 (azulenium) and 5.01 ppm (benzene) as well as those due to benzene (ca 7.0) and azulenium ion (8.87 ppm). The two singlets disappeared in 15 min to give new signals at 3.83 (t) and 4.33 ppm (dd). If CF_3CO_2D was used as an acid, the latter disappeared and the former became a singlet. Thus, the structure of the product 36 and the pathway of its formation are suggested as shown. We are now trying to isolate 36 or its derivatives.



36

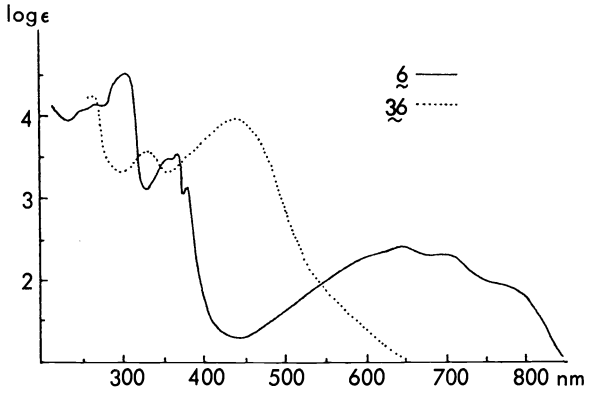


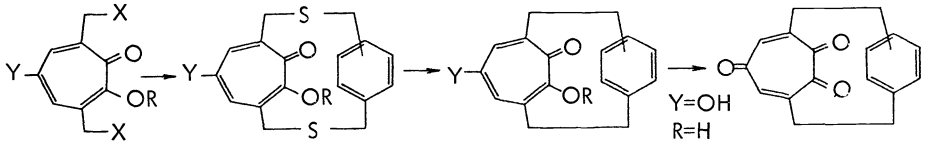
Fig. 13. Electronic spectra of 6 (in cyclohexane) and 36 (in CF_3CO_2H).

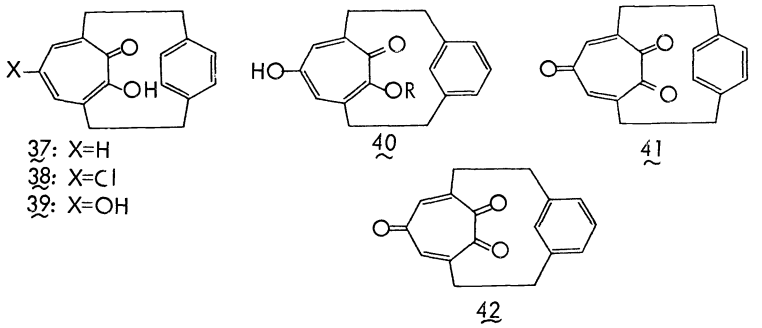
PHANES CONTAINING TROPOLONE AND TROPOQUINONE

Our main interest in these compounds are naturally directed to the question: How and to what extent various physical properties and chemical behaviors demonstrated by the monocyclic counterparts are modified when two distant positions are connected by a short bridge? Although [7] and [8](3,7)-tropolonophanes (26) and [2]paracyclo- and [2]metacyclo[2](3,5)tropolonophanes (27) have been synthesized in our laboratory, the present discussion will be confined to tropolonophanes and p-tropoquinonophanes with the bridges at 3- and 7-positions of 7-membered rings.

Synthesis

Tropolonophanes were synthesized via "sulfur route" starting from 5-substituted-3,7-bis(chloromethyl) tropolones. Since these compounds are unstable under the coupling conditions, the hydroxyl groups have to be protected as methylether. Thermal decomposition of disulfones is always the method of choice for extrusion of sulfur. Tropoquinonophanes were prepared by the oxidation of the corresponding hydroxytropolonophane. Thus the following tropolonophanes (28, 29) and p-tropoquinonophanes (29) have been synthesized, along with some of dithia homologs.





Geometries

All of these [2.2]phanes have fixed geometries at least on NMR time scale, as judged from the bridge proton signals in PMR spectra, while their dithia homologs display rapid conformational changes. Although the 7-membered rings in 37-40 takes the tropolone form as judged from their NMR spectra, the ring in 37 is bent considerably as shown by X-ray crystallographic analysis (Fig. 14) (28).

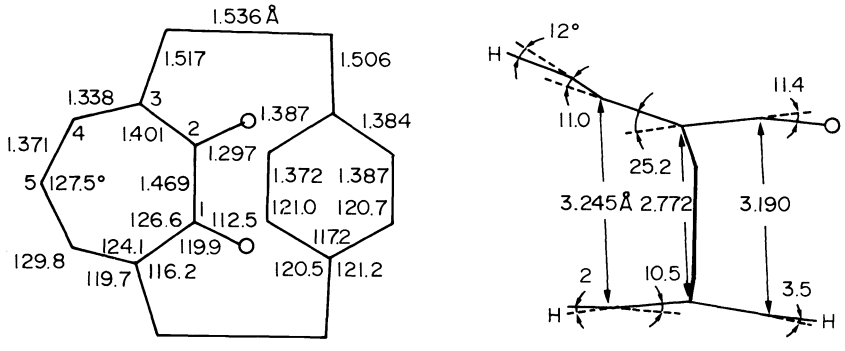
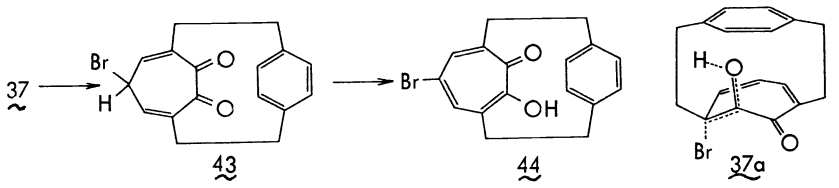


Fig. 14. Molecular geometry of 37 as determined by X-ray analysis.

Reactions of tropolonophanes

Although 37 and 38 behave generally in the same way as the corresponding open chain tropolones do, the effect of the deformation due to the strain emerges in some cases. Thus, catalytic reduction of 38 to 37 is always accompanied by over-reduction, and bromination of 37 (1 eq. Br_2, dil. HOAc, 0°, 1 hr) gives 43 with a diketo structure in quantitative yield. On heating crystals or in t-BuOH, 43 changes to the bromotropolone 44.

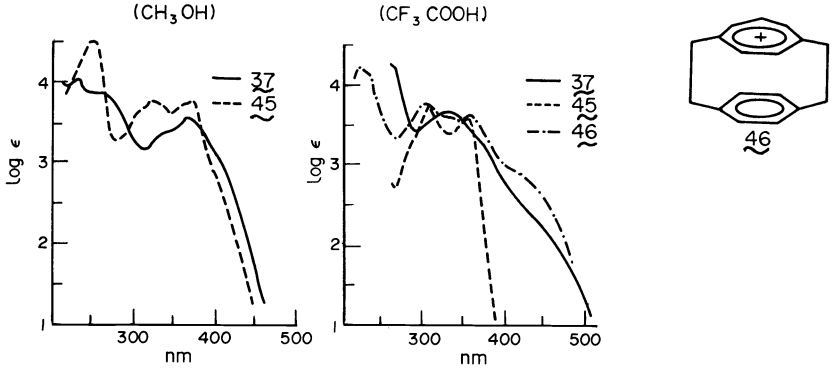


43 44 37a

Since 3,7-dimethyltropolone 45, the reference compound, gave under the same conditions xylenols (the products of C_3-bromination) and 5-bromo-3,7-dimethyltropolone in the ratio 3:1, the absence of C_3-bromination in 37 may also reflect the steric compression in its transition state leading to the corresponding phenol. As shown in 37a the transition state should have one of the oxygens close to the benzene ring.

CT interaction

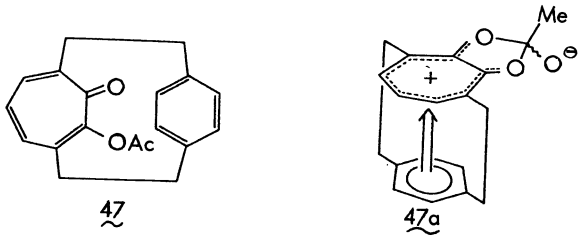
As in azulenophanes, CT band is not observed clearly in the UV spectra (Fig. 15) of tropolonophanes in neutral media. However, in strongly acidic media, a weak bond appears at ca 450 nm as a shoulder. Since no such an absorption is present for 45 under the same conditions and similar absorption was observed for tropyliophane 46 (30), it is probably due to CT interaction.



46

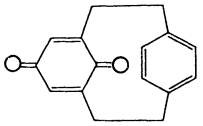
Fig. 15. Electronic spectra of 37, 45 and 46.

The same interaction seems play a substantial role in the reaction in which positive charge develops in tropolone ring. Thus, activation energy for the acetotropy in the acetate 47 ($\Delta G^{\neq}$=8.7 kcal/mol) is significantly smaller than that in tropolone acetate ($\Delta G^{\neq}$=10.8 kcal/mol) (31). The transition state would be stabilized as shown in 47a shown below.

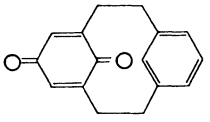


47 47a

The electronic spectra of tropoquinonophanes 41 and 42 (Fig. 16), show a shoulder at ca 400 nm, compared with 3,7-dimethyl-p-tropoquinone 48. The similar shoulders are observed (Fig. 17) also in the corresponding benzoquinonophanes 49 and 50 (29). Electron affinity of 41 and 42 (E_A=0.77 eV for both) obtained from polarographic data is considerably smaller than that (E_A=1.06 eV) of 48. The reduced electron affinity is due probably to a large extent to the CT interaction because similar decrease ($\Delta E_A \doteqdot 0.2$ eV) is observed for 49 and 50 (E_A=0.56 and 0.54 eV, respectively) compared with that of 2,6-dimethyl-p-benzoquinone 51 (32). The difference in the decrease would be originated from the larger deformation of tropoquinone ring in 41 and 42 than benzoquinone in 49 and 50. Such a deformation in 41 is clearly indicated by our preliminary X-ray analysis.



49



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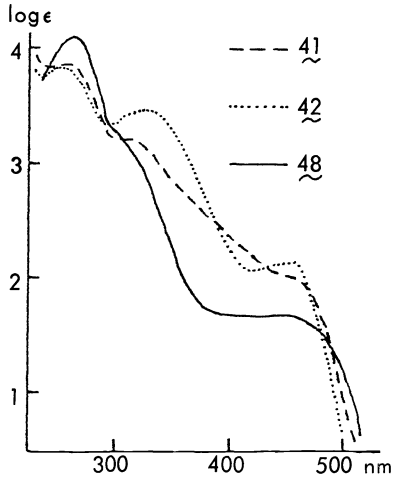


Fig. 16. Electronic spectra of 41, 42 and 48.

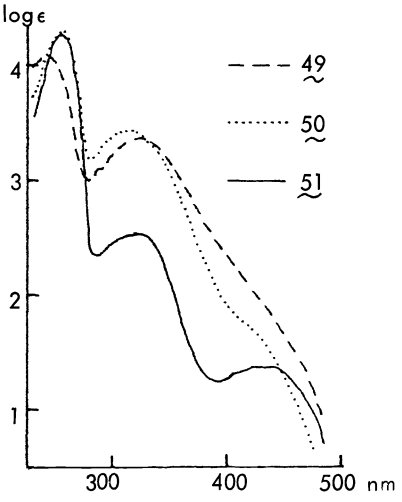
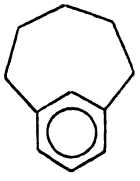


Fig. 17. Electronic spectra of 49, 50 and 51.

[4](2,7)TROPONOPHANE

The problem in the single-decked phanes is how far we can reduce the length of bridge without changing basic nature of parent compounds and how the basic nature is modified in the resulted compounds. In metacyclophane series, the shortest bridge known is C_5 in [5]metacyclophane 52 synthesized by Bickelhaupt (33), while in paracyclophane it is C_6 (34). The next lower member in the former series, [4]metacyclophane, is not known, the attempt resulting in the formation of its Dewar isomer 53 (35). In the troponophane series, [6](2,7)troponophane 54 (36) is the smallest known bicyclic member of the meta-type, although in the benzotroponophane, tetramethylene compounds 55 (37) and 56 (38) have been prepared or recognized as a reactive intermediate. We have recently succeeded in synthesizing bicyclic [4](2,7)troponophane 57 and its dehydro analog 58 (39), which show extensively modified physical properties of tropone.



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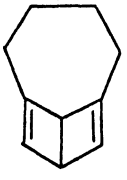
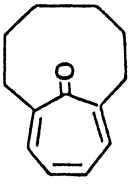


53



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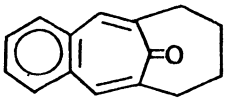

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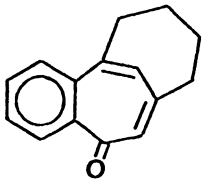
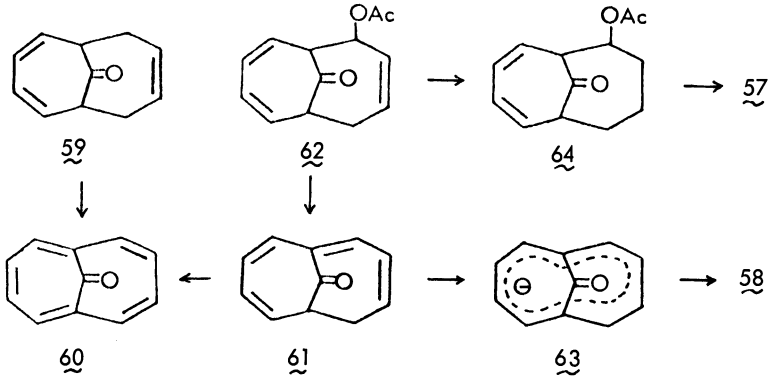


56

58

Synthesis

We have known for some time (40) that the tropone-butadiene adduct 59, our starting material for the synthesis of 1,6-methano[10]annulene-11-one 60, can be deuterated at both α-positions to the carbonyl group. When the dihydroannulenone 61 (41), another starting material to 60, derived from the tropone-acetoxybutadiene adduct 62, was treated with KOtBu at -80° in tBuOH and THF, dark red solution, probably due to the delocalized 10π anion 63, was resulted. Acidification and purification afforded 58, m.p. 84-86°, in 67% yield. In a similar way, troponophane 57, m.p. 61.5-63°, was synthesized in good yield starting from 62 via 64.



X ray analysis

Their structures were established beyond any doubt by X ray analyses. The molecular dimensions of 57 are shown in Fig. 18 as an example. The most remarkable structural feature of 57 compared with that of tropone (42) is naturally a tub-shaped tropone moiety. It is more deformed than in tropylidene (43) and even than in 55 (44). A simple and straight forward implication of this feature is the reduced conjugation of the carbonyl group. This is clearly shown by the following spectra.

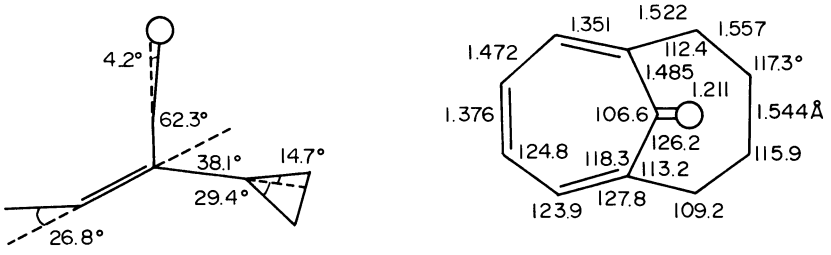


Fig. 18. Molecular dimensions of 57.

NMR spectra

All protons in the tropone part of 57 and 58 resonate at much higher field than in 2,7-dimethyltropone 65, and [9](2,7)troponophane 66 (45). Comparison of the PMR and CMR chemical shifts with the related compounds (Fig. 19), revealed the following remarkable features. On going from the open chain tropone 65 to the short-chain troponophanes 57 and 58 through longer-chain troponophanes 66 and 54, there are regular changes both in PMR and CMR that β-H and β-C, as well as α-C show large up-field shifts while γ-H and γ-C change a little. Thus in 57 and 58, β-H and β-C appear at higher field than in the γ-counterparts, the situation very similar to that of 2,6-dimethyltropylidene 67 (46) and the corresponding phanes 68 with saturated bridge (46) and 69 with unsaturated bridge (47). The carbonyl carbon shows a large down field shift on going from 65 and 66 to 57 and 58.

Electronic spectra (Fig. 20)

The strong band at ~310 nm in the UV spectra of planar tropones is reduced in those of 57 and 58 to weak shoulders, intensity of which are comparable with those of the isolated carbonyl group. The position of the stronger peaks (250-260 nm) is very similar to that of the tropylidenophane 68 (46). The spectrum of 57 is somewhat different from that of 55 (37) which exhibits a single maximum at 226 nm.

IR spectra

In accord with the famous precedences of benzotropone series (37) in which 55 is reported to have a carbonyl band at 1724 cm^{-1}, both 57 and 58 exhibit carbonyl bands at 1718 cm^{-1}, as is expected from the carbonyl bond angle of 107°. Thus all of these spectra shows a very small effect of conjugation.

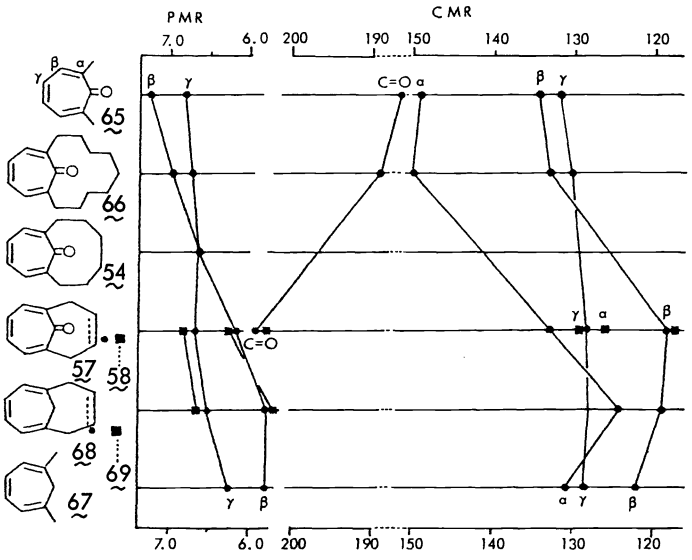


Fig. 19. PMR and CMR chemical shift of troponophanes and the related compounds.

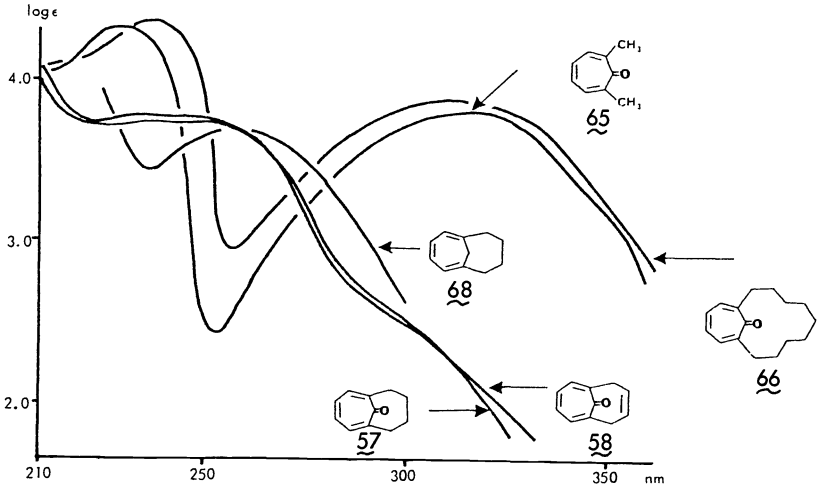


Fig. 20. Electronic spectra of troponophanes and the related compounds.

Mass spectra and decarbonylation

Mass spectra of 57 and 58 show base peaks correspond to [M-CO], along with small molecular ion peaks. The suggested facile decarbonylation was confirmed by heating them to 200°, whereby tetralin and 1,4-dihydronaphthalene were obtained, respectively. This reaction is taken as the reflection of the nonplaner conformation in 57 and 58. Tropone needs at least 500° to decarbonylate (48).

Stability of 57 and 58, as well as 55 compared with 56 is most probably due to the lack of double bond character in the bridging bond. It is therefore tempting to observe any indication of the double bond character at the bridging bonds. Studies in this direction as well as on the chemical behavior of 57 and 58 are in progress.

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