

SOME ASPECTS OF STRAINED SYSTEMS. [4]ANNULENE AND ITS CH⁺ ADDUCT

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ABSTRACT

The application of a set of criteria based on quantum chemistry very often predicts the possible existence of unique organic species that are never conceived in classical organic chemistry. The square pyramidal adduct of [4]annulene of C_{4v} symmetry is a good example and has been well characterized. In contrast, the quantitative evaluation of strained systems by means of the most recent theoretical treatments appears to be still inadequate, particularly in the case of unstable species surrounded by low energy barriers. [4]Annulene, a century-old problem, illustrates the current state of theoretical development. The properties of a derivative of [4]annulene, perturbed slightly by substituents, methyl tri-*tert*-butyl[4]annulenecarboxylate, has now been fully elucidated, including its x-ray crystallographic analysis. Thus, the first unambiguous direct evidence has been secured to demonstrate that a rectangle, distorted slightly by substituents, corresponds to the most stable conformation of this [4]annulene system. It is now almost certain that the ground state of the parent [4]annulene is singlet. Evaluating all the experimental evidence available at present, it is most likely that [4]annulene is rectangular with two short bonds of approximately 1.37 Å and two longer ones of the order of 1.51 Å. Should this compound turn out to be square, both square and rectangle must reside in a region of a flat potential surface.

INTRODUCTION

There are, in the history of chemistry, few rules that have withstood experimental tests as extensively as Hückel's $(4n + 2)$ postulate¹. This is indeed remarkable, in view of the bold assumptions which were utilized in formulating this simple rule. With the availability of efficient computational facilities in recent years, there have appeared numerous attempts to improve the theoretical treatment of organic compounds, and the σ bond is now taken into consideration as well. At the same time, improvements of experimental techniques have brought about important experimental evidence to prove or disprove conclusions that are theoretically predicted. The problems associated with the $(CH)_4$ species and related compounds are very timely and represent a challenge to both theoreticians and experimentalists. This species is theoretically complicated and also requires demanding experimental techniques. We have been engaged in a rather broad subject, namely, the chemistry of $(CH)_n$ and $(CH)_n(CH)_{2m}$ species, and the $(CH)_4$ species is the one that we have studied most intensively in recent years. I have chosen two topics; (i) the CH⁺ adduct (1) of [4]annulene, to demonstrate how

powerful and useful the theoretical guide has been to the experimentalists and, (ii) [4]annulene (2) itself, to illustrate the extent of validity of recent calculations as viewed and felt by an experimentalist.

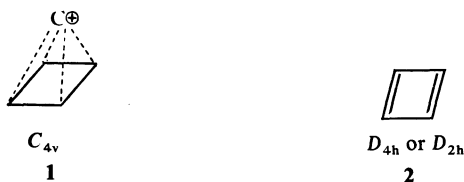


Figure 1

SQUARE PYRIMIDAL CATION

As a logical extension of quantum chemistry, the application of a set of a few simple criteria has proved to be very useful in predicting the stability of certain species. An example is the square pyramidal cation (1)², a species never conceived in classical organic chemistry. Suppose that we have two segments and that we wish to consider whether or not coupling of these segments would lead to a stable species. It is obvious that the following three factors must be considered for effective coupling: (1) the relative energies of the orbitals involved in the coupling, (2) symmetry properties and (3) the magnitude of overlap (geometry).

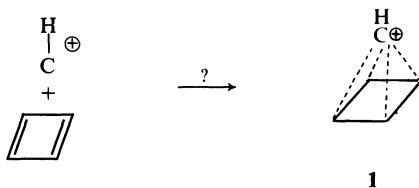


Figure 2

Application of these criteria to (1) is shown opposite: Three orbitals of the positively charged methine are shown on the left side and those of [4]annulene on the right. The exact levelling of the two orbitals of the latter is not critical in the present discussion. All that is required is that the two are of almost equal energy and are in the same level as that of the *p*-orbital of the methine. From this diagram it is clear that three pairs of orbitals will interact very effectively to result in a stable species, the square pyramid. Stohrer and Hoffmann also suggested that interconversion of one C_{4v} cation to another (degenerate isomerization) would proceed through a low energy barrier such as the homotetrahedranyl cation, the C_{2v} cation (3). Although it may appear very simple and straightforward to devise experiments to endorse this prediction, the acid- and thermal instability of this type of strained system presented an enormous amount of difficulty. I shall discuss our results as briefly as possible in the following

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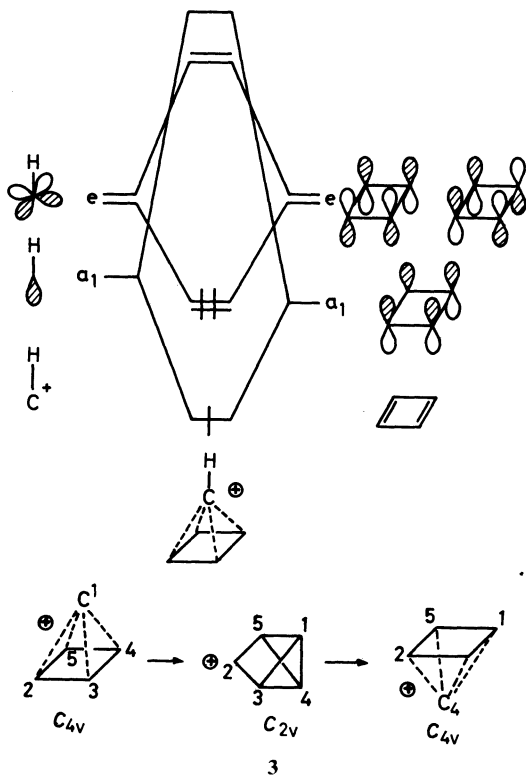


Figure 3

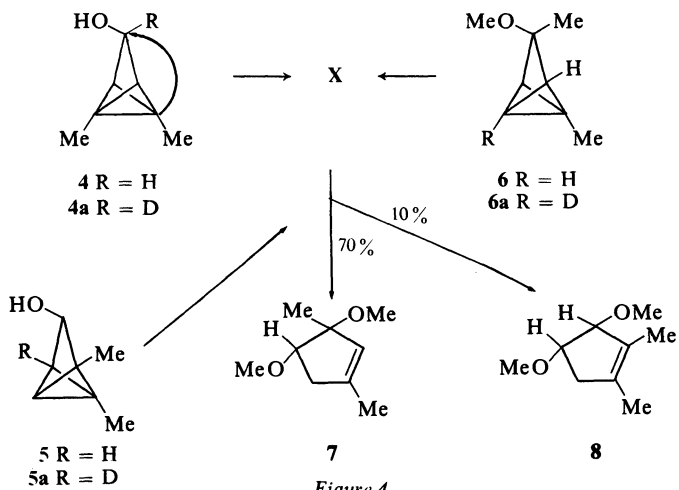


Figure 4

manner. Three differently, but specifically substituted hydroxy or methoxy homotetrahedrane derivatives (4), (5) and (6) were prepared³. Solutions of these compounds in a 3:2 mixture of SO_2ClF and FSO_3H at -80° , all provided identical p.m.r. and c.m.r. spectra which remained unchanged for several hours. Quenching the acidic solutions obtained from either (4), (5) or (6) with cold methanol containing excess sodium methoxide afforded the same mixtures of (7) (70 per cent yield) and (8) (10 per cent), in addition to other unidentified minor products⁴.

If the formation of the square pyramid does proceed in a stereospecific manner, namely a carbon atom *anti* to the leaving group becoming an apical centre of the square pyramid as indicated by the arrow, then (4), (5) and (6) should all form the same cation. The n.m.r. spectra of the cation are shown below:

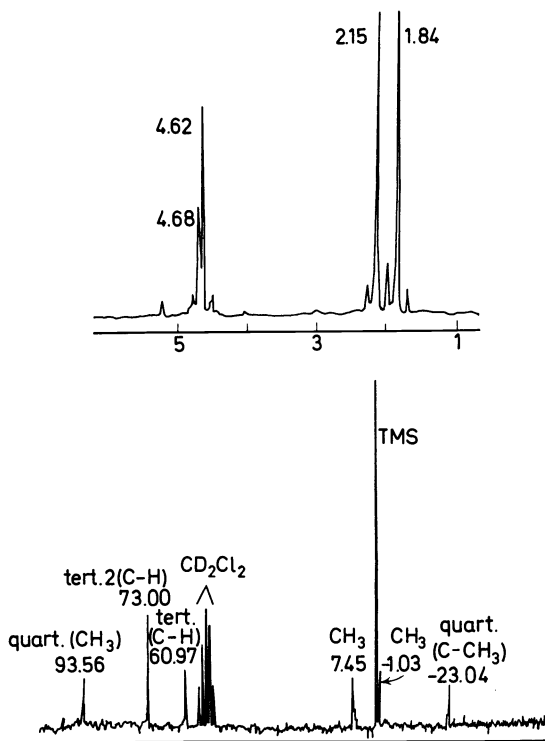


Figure 5

Both the proton and ^{13}C spectra indicate the presence of twofold symmetry. An off-resonance spectrum allowed the assignment of the ^{13}C signals to two quaternary carbons (one at extremely high field), two equivalent methines, an additional different methine, and two different methyl groups. Note that in the ^{13}C spectrum there is no signal at low field, there are two equivalent CHs, and one of the quaternary carbons appears at an extraordinarily high field. Several possibilities must be considered for the structure of this cation:

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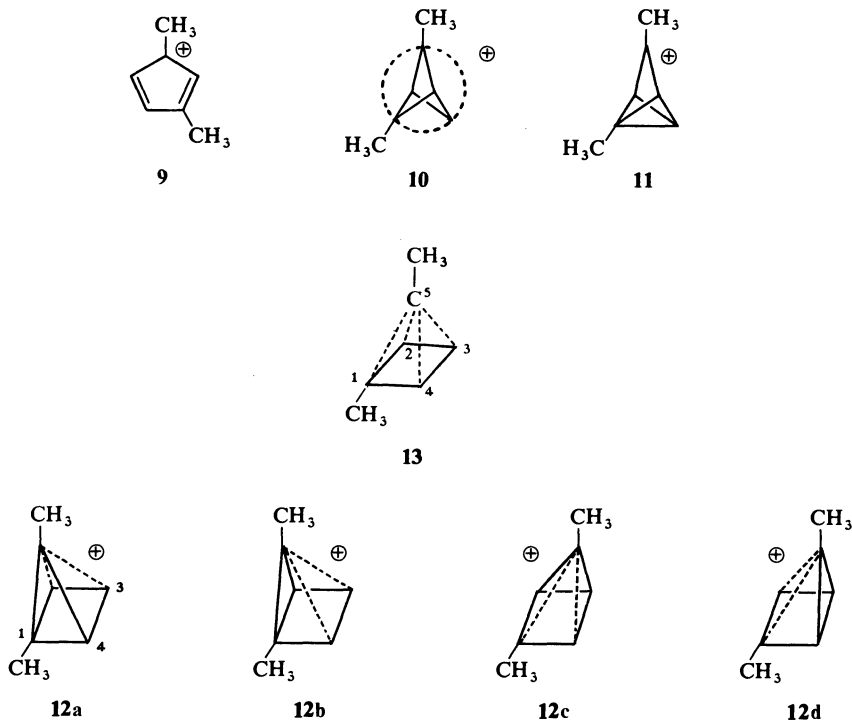


Figure 6

In short, the appearance of two non-equivalent CH_3 signals in the p.m.r. and c.m.r. spectra immediately eliminates the cations (9) and (10) as possible structures for the cation. The absence of any low field absorptions in the c.m.r. spectrum excludes a charge-localized structure such as (11), even though the cationic centre is tertiary. Of the three methine (CH) groups appearing *at almost the same field, two are equivalent*, thus excluding a non-equilibrating unsymmetrical, single species such as (12a). Thus, the evidence strongly indicates that the correct representation of the cation is either a mixture of rapidly equilibrating ions (12a-d) or a single, highly charge-delocalized species expressed by square pyramid (13). We can thus assign all the signals, as shown overleaf:

The signal assigned to the apical carbon appears at extremely high field, indicating that there is little residual positive charge, if any, at this carbon atom and that the orbitals associated with this particular carbon are extremely constrained. Initially, this appeared to be very unusual to us, but since then we have observed that several other compounds exhibit similar high field absorptions (*vide infra*). When a deuterium atom is incorporated into the precursor at a specific position, the signal corresponding to that position in the cation disappears in the p.m.r. spectrum. This demonstrates that the facile skeletal rearrangements predicted and discussed earlier do

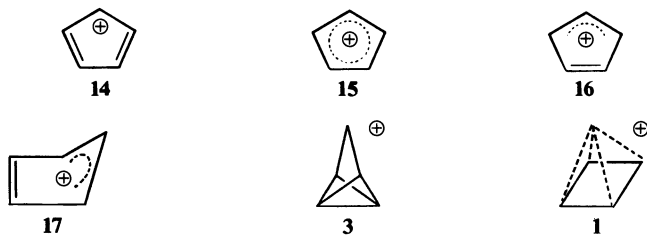
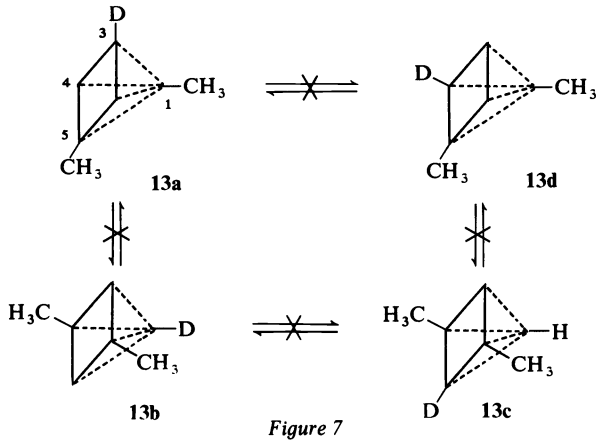
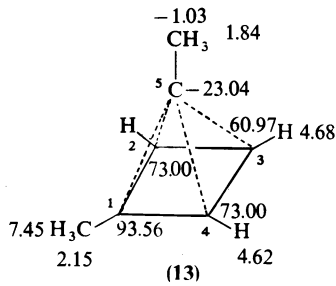


Table 1

Relative energy	5a → d		CINDO-2 corrected for strain	MINDO-3	ab initio STO-3G	4-31G
	Relative energy	CINDO-2				
14	54	10	1.9	21.4	18.1	
15	54	10	13.1*	0	0	
16	54	10	1.5	20.6	21.4	
17			0			
3	27	30	34.4	>44.8	>71.0	
1	0	0	14.1	44.8	71.0	

* 13.1 for singlet, -1.6 for triplet.

not proceed in this case. For instance, conversion of (13a) into (13d) presumably via (13b) and (13c) encounters an appreciable energy barrier. Therefore, the question as to which is more stable, cation (13) with one apical or one basal methyl group or a square pyramid with two methyl groups at basal positions such as (13b) has not been answered experimentally. The square pyramid obviously belongs to the $(\text{CH})_5^+$ species. Other important members of this group are tabulated opposite.

Several calculations⁵ have appeared and all agree at least on one point: square pyramid (1) represents an energy minimum surrounded by relatively high walls. This is now experimentally verified, thus Stohrer and Hoffmann's initial prediction has indeed brought with it a new and intriguing feature into carbonium ion chemistry. However, if one examines the table a little more carefully, one will find that there are several discrepancies among these treatments. Most important of all is the question as to which is more stable, the cyclopentadienyl cation (14) or the square pyramid (1). The *ab initio* 4-31G calculation shows that the square pyramid (1) is very unstable with respect to D_{5h} (15) by 71 kcal/mol. Both species have now been prepared. However, cation (15) is very reactive even at low temperatures and presumably polymerizes very readily. The dimethyl derivative of (1) was warmed up to -20° but there was no indication that it underwent any rearrangement. Thus, a determination of the relative energy of (15) and (1) as well as an estimate of the energy barrier intervening between the two species awaits further studies. It is interesting to see that six electrons (a Hückel 'magic number') are used to stabilize the system and thus (1) is a unique 'aromatic' compound.

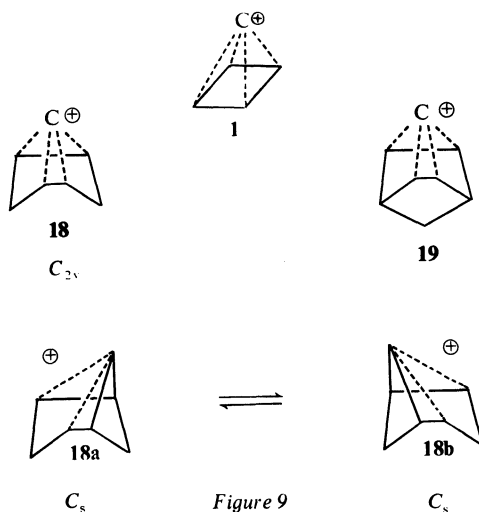


Figure 9

It is pertinent to discuss an extension of this concept of orbital coupling. Two cations chosen for this purpose are (18) and (19), both having C_{2v} symmetry.

In both cases, the cyclobutadiene moiety of (1) is replaced by cyclohexa-1,4-diene. The structure of (18) may well be represented by a rapidly equilibrating mixture of (18a) and (18b) of lower symmetry (C_s). These cations correspond to the trishomocyclopropenium cation which has been prepared and directly observed in our laboratory previously⁶. The energy profile of (18) can be easily drawn as a function of the dihedral angle α as shown below⁷.

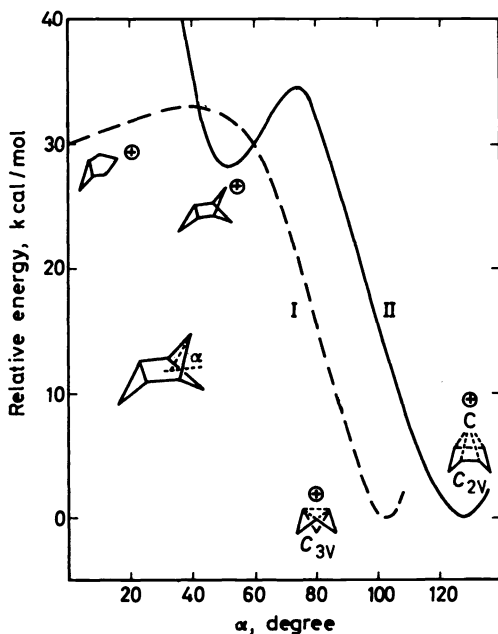


Figure 10

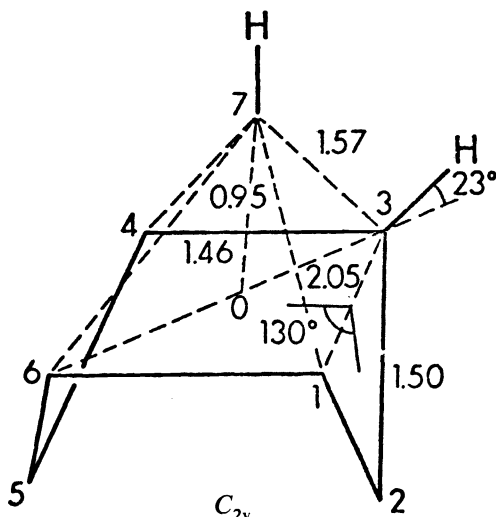


Figure 11

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Cation (18) possesses two energy minima, one corresponding to a cyclobutonium cation and the other to the C_{2v} structure. On curve II, one does not observe an energy minimum which corresponds to the trishomocyclopropenium cation (C_{3v}), the true minimum of curve I. MINDO-2 was used for the calculations and the geometry was optimized at the energy minima. The calculated geometry of cation (18) is shown above. The apical carbon 7 is well within a bonding distance from the basal carbon atoms 1, 3, 4 and 6 (1.57 Å), but somewhat surprisingly, the distance between carbons 1 and 3 is as large as 2.05 Å. The hydrogen atoms attached to the basal carbons are bent upwards so that the π -orbitals of cyclohexa-1,4-diene can accept the p -orbitals of the apical carbon effectively.

Compounds (20) and (21) chosen as precursors of the cation (18) provided the same n.m.r. spectra⁸. When solutions containing the cation were quenched, the methoxy compound (23) was obtained.

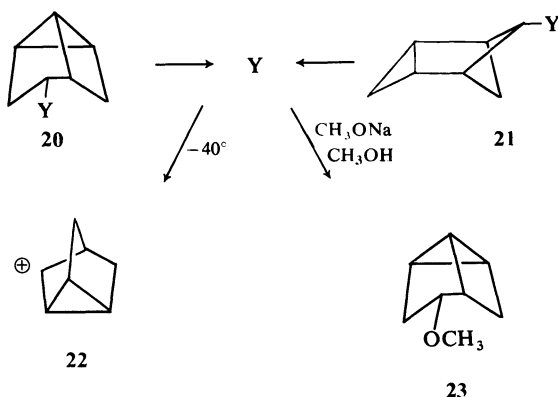


Figure 12

The cation which was prepared at -110° underwent rearrangement at -40° to yield (22) whose structure was confirmed by generating the same cation from an appropriate precursor. Both the p.m.r. and c.m.r. spectra shown below clearly demonstrate the presence of twofold symmetry in the cation and again a unique signal at very high field, assigned to the apical carbon appears in the c.m.r. spectrum.

The cation (24) shown overleaf is very similar to (18). Carbons 1 and 4 are now linked together by a methano bridge. We conducted this experiment⁹ simply because calculations predict that the positive charge will accumulate at the apical position, as the distance between carbons 2 and 5 of (18) becomes shorter.

Both precursors (25) and (26) of (24) were processed in a similar manner to provide the cation whose n.m.r. signals are indicated in (24). The chemical shift of the apical carbon now appears at δ 2.4 as compared to δ -17.15 observed for the corresponding carbon atom of the non-bridged cation (18). Upon quenching this cation with sodium methoxide in methanol, the nucleophile attacked both the basal and apical centres to provide the

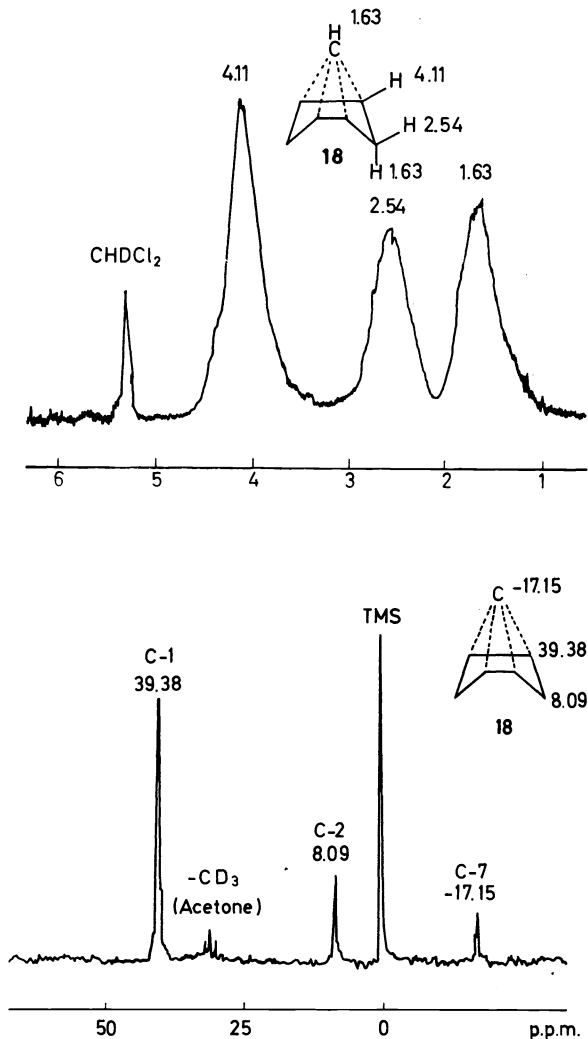


Figure 13

methoxy derivative corresponding to **(25)** and **(26)**. This is in contrast to the observation with **(18)** where the attack took place only at the basal carbons. Whether or not these two experimental facts, viz. (1) the downfield shift of the apical carbon signal, and (2) the mode of nucleophilic attack, in fact reflect the increase of charge at the apical centre as predicted by theory, the results are very gratifying.

I believe that the above examples which I have discussed at some length have clearly shown that the application of the simple orbital coupling concept, leads to new and interesting types of species. The factors or conditions which are required for effective coupling (*vide supra*), certainly reflect

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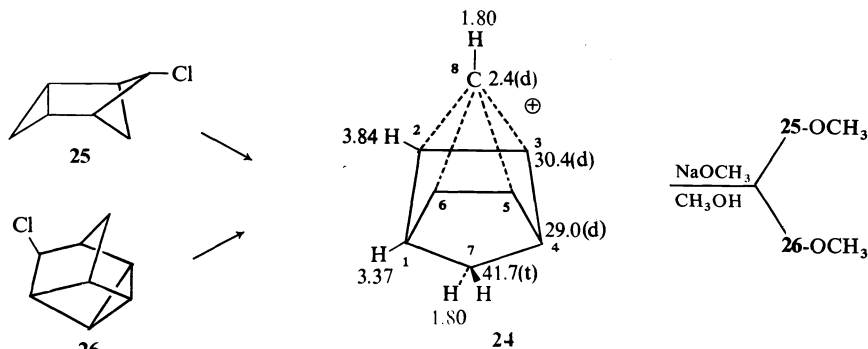


Figure 14

the result of various approximations, and in many cases theory and experiments are mutually consistent, at least qualitatively. We are now engaged in the investigation of many other equally interesting species, and preliminary calculations by means of standard programmed procedures as MINDO-2 are serving as a guide, of course, with great caution being exercised in evaluating the quantitative aspects of the calculated results.

[4]ANNULENE

In contrast to the previous cases that are concerned with deep energy minima, the theoretical treatment of unstable species that are surrounded by low energy walls present rather inconsistent overall pictures. [4]Annulene (2) is a good example and is certainly a theoretically very complex molecule comprising eight atoms. Table 2 shown below lists several calculations that have appeared in the past ten years. There are three possible structures conceivable for (2), two singlets, rectangular or square, and a square triplet. Except for two calculations, an earlier one^{10b} and the most recent^{10f},

Table 2. Theoretical treatments of [4]annulene

Author	Method	Relative energy			Reference
		R($\uparrow\downarrow$)	S($\uparrow\uparrow$)	S($\uparrow\downarrow$)	
Dewar (1965)	PPP π -approx.	0	14.1	—	10a
	SPO π -approx.	0	22.1	—	
Allinger (1968)	PP-Cl π -approx.	6.1	0	—	10b, c
	PP-Cl (singly excited Cl)	0	1.8	18.0	
	PP-Cl (doubly excited Cl)	0	15.3	4.8	
Buenker (1968)	<i>Ab initio</i> -Cl (six config.)	0	~ 10	~ 15	10d
	<i>Ab initio</i> -Cl (extended Cl)	0	~ 24	~ 10	
Dewar (1971)	PPP (half electron treatment for triplet)	0	2.0	16.4	10e
	MINDO-2	0	—	16.6	
Newton (1973)	GVB	less stable	0	7.7	10f
	4-31G	?	most stable(?)	?	

Figure 15

all the treatments appear to agree on one point: the rectangular singlet is more stable than its square counterpart. In the square geometry the relative stability of singlet and triplet appears to be uncertain. The most recent treatment^{10f} which was apparently carried out to conform to the result obtained from the infra-red spectrum of (2) concludes that the square triplet is the most stable species of the system, and lies 7.7 kcal/mol below that of the square singlet. Information concerning this calculation is limited and somewhat unclear, however. *Figure 16* summarizes all these results.

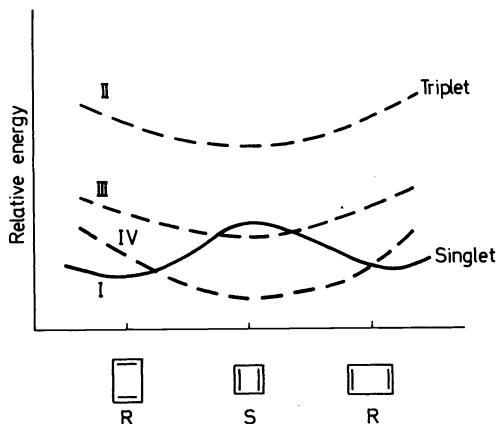


Figure 16

The solid line (I) indicates that the energy curve of the singlet state has two minima at the rectangular (R) geometry and a flat maximum in the square (S). The dotted lines (II-IV) follow the triplet energy and may lie well above the singlet, (II). If the triplet state has a minimum with the square geometry, then the minimum may or may not lie below that of the singlet energy [(IV) and (III) respectively]. It is difficult to evaluate these calculations, but we may be able to provide some experimental evidence to settle this controversy. Allinger^{10c} calculated (see below) the ultra-violet absorption maxima that (2) is likely to exhibit and quite confidently predicted that a singlet (2), whether square or rectangular, has allowed transitions around 200 nm, and weak forbidden transitions at much longer wavelengths in the visible region. In contrast, the triplet (2) will absorb very strongly ($\epsilon \sim 10^3$ at 380 nm). He stated that this difference will serve to distinguish between the singlet and the triplet ground states.

The ground state properties and the methods for determining these are summarized: (1) geometry by x-ray analysis, (2) spin state by means of e.s.r. spectra, (3) electronic states by ultra-violet spectra, (4) magnetic properties from the chemical shifts of a proton attached to the system, (5) vibrational modes by infra-red and Raman spectra and, (6) ionization potentials by photoelectron spectra. If (2) were unreactive enough to allow us to isolate it in a crystalline form, the history of its chemistry would never have lasted for a century. We have taken two approaches, (1) the preparation of the

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Table 3. Calculated spectra of cyclobutadiene (Pariser-Parr approximation with doubly excited configuration interaction)^{10c}

Molecule	Transition energy (nm)	<i>f</i>
S(↓↑)	722.8	0
	210.8	0.09
	204.1	0
	150.9	0
S(↑↑)	134.0	0.39
	406.8	0.01
	379.4	0.2
	176.2	—
R(↑↓)	175.7	—
	506.5	0
	471.3	0
	197.7	0.21
	171.8	0.01
	136.6	0
	125.2	0.88

Figure 17

parent compound at low temperatures and, (2) the synthesis of a derivative in which the electronic state of (2) is least perturbed, yet its reactivity is suppressed by sterically blocking the approach of another molecule thus allowing its isolation in a crystalline form. Most importantly, the substituents are chosen in such a way so as to preserve symmetry in an important way. Data accumulated in recent years have shown that tri-*tert*-butyl[4]-annulene (27) and its methoxycarbonyl derivative (28), appear to fulfil the above conditions and we therefore decided to synthesize these compounds. Compound (29) which was elegantly synthesized by Kimling and Krebs¹¹, has a drawback in that the substitution pattern is such that the two bonds sharing one carbon atom of [4]annulene are not equivalent as far as the π -electrons of the system are concerned. The exact geometry of compound (29), even if elucidated, would provide little information as to the geometry of the parent compound. For the sake of convenience, I wish to discuss first the chemistry of the substituted [4]annulenes and then that of the parent compound.

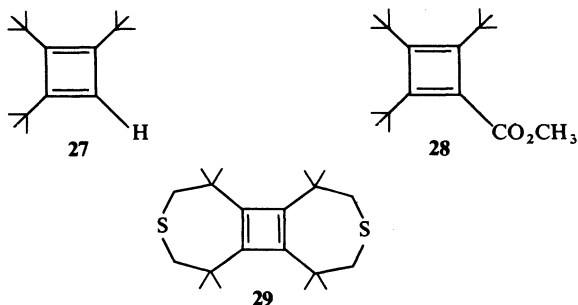


Figure 18

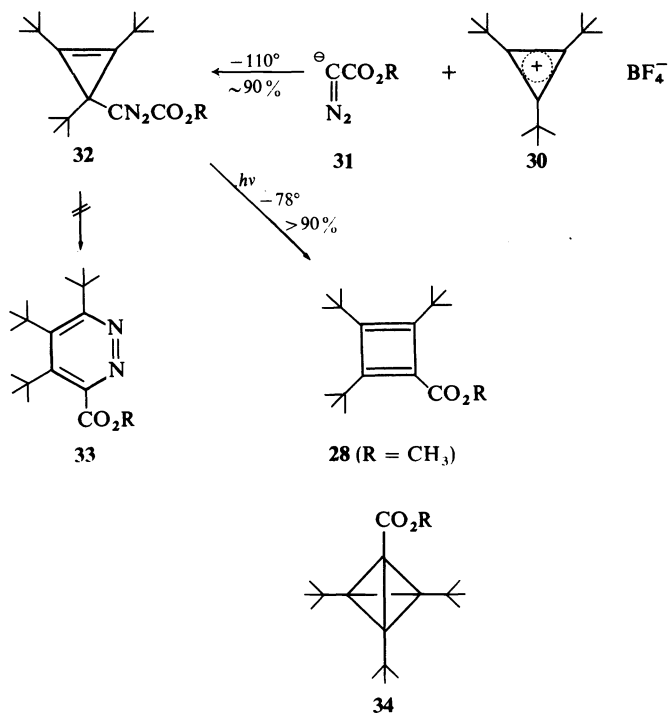


Figure 19

We have extensively examined a number of routes leading to the compound (28) and have more or less serendipitously found that the well-known ring expansion method utilizing cyclopropenylmethylene does indeed proceed remarkably well with highly substituted precursors¹². The reason for this unexpected success is partly that the normal route leading to (33) is now blocked by the crowding of the three *tert*-butyl groups of (33). Compound (32) is a remarkably stable compound and was obtained by reacting tri-*tert*-butylcyclopropenium fluoroborate (30) with the anion of the diazo ester (31). Photolysis of (32) in oxygen-free pentane proceeded smoothly, and when a 1 M solution was irradiated, a large amount of crystalline precipitate formed which was recrystallized from pentane to afford light brown needles. Compound (28) sublimed very easily at 50° under reduced pressure, thus eliminating the possibility of the product being a dimer. N.m.r. spectra demonstrated the presence of twofold but not threefold symmetry, therefore precluding the possibility that the compound is (34). Not surprisingly, in view of Krebs's result, compound (28) is thermally stable but it reacts immediately with oxygen.

The following summarizes the results of both the p.m.r. and c.m.r. spectra of (28). To the limit of the n.m.r. time scale, two *tert*-butyl groups are equivalent, and also three annular carbon atoms of the system exhibit a signal at the same field. The chemical shifts of the ring carbon atoms appear to be low but

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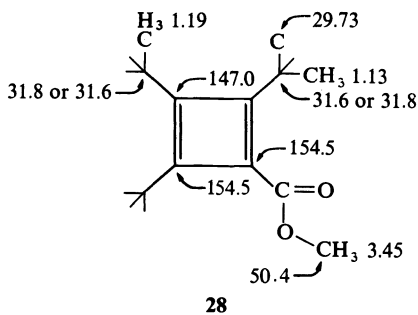


Figure 20

they are not exceptional if one considers the presence of the substituents and the unique geometry of the system.

In order to confirm the assigned structure (28) and to test the reactivity of the system, the following chemical conversions have been performed. Reaction with maleic anhydride led to the quantitative formation of an

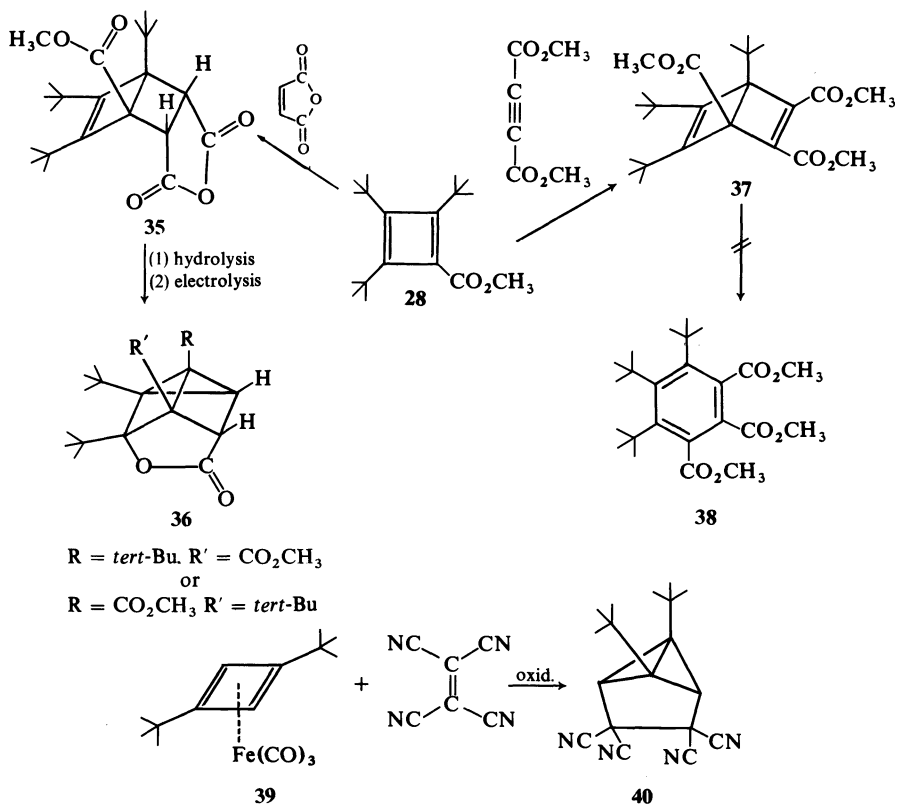


Figure 21

adduct which is formulated as (35), but not as a dihydrobenzvalene derivative. Incidentally, 1,3-di-*tert*-butyl[4]annulene oxidatively generated from its $\text{Fe}(\text{CO})_3$ complex (39) reacted with tetracyanoethylene in a 2 + 2 + 2 fashion to give (40)¹³. Hydrolysis of (35) to the corresponding dicarboxylic acid followed by electrochemical decarboxylation afforded compound (36) providing evidence for the *endo* configuration of the acid anhydride group of (35). Acetylenedicarboxylate reacted similarly to yield compound (37). Not surprisingly, attempts to ring open this Dewar benzene into the corresponding benzene derivative failed. Thus, the above spectral and chemical evidence establishes the structure of (28). This compound is extremely valuable in that it is highly crystalline and is subject to x-ray analysis. However, before we discuss the geometry of this compound, I wish to outline the synthesis of compound (27) which carries a proton directly attached to the system.

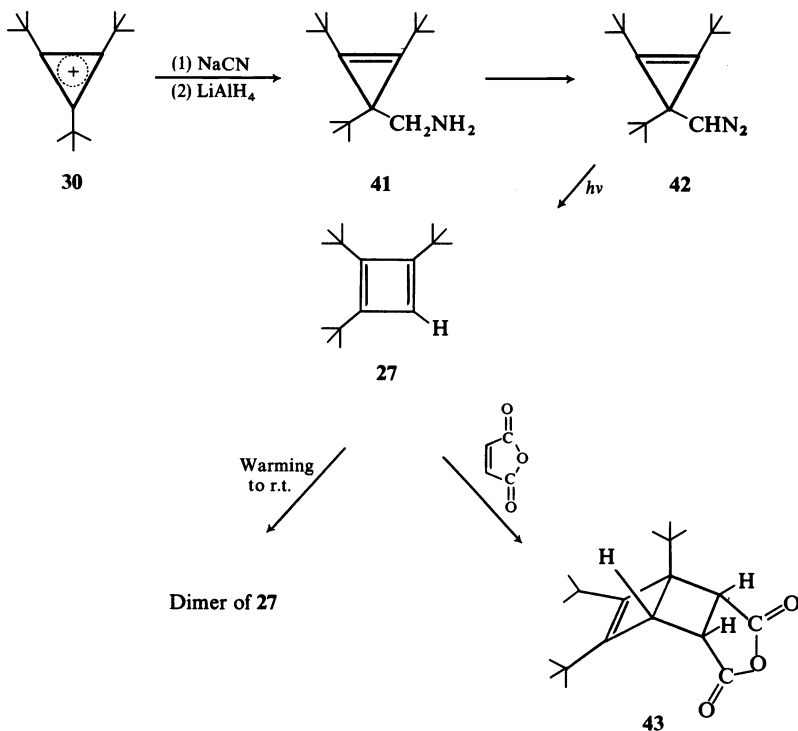
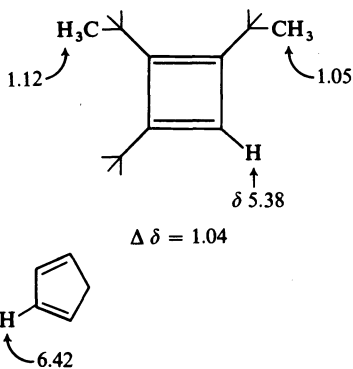


Figure 22

Carbon n.m.r. absorptions are relatively insensitive to ring current effects even when the carbons are uniquely positioned in the system to detect these effects¹⁴. For this reason, ¹³C signals which are due to annular carbons provide virtually no information about the ring current. Compound (27) has been synthesized in a manner similar to that already discussed. Compound (30) was converted into the corresponding cyano derivative which in

turn was reduced with lithium aluminium anhydride to provide an amine (41). The diazo compound (42) was prepared from this amine in the usual manner and the photolysis of (42) either in methylcyclohexane or tetrahydrofuran at -70° provided the desired (27). Although the reactivity of (27) compared to the corresponding methoxycarbonyl compound precluded further purification, the p.m.r. signals that are shown below are evidently due to compound (27). Reaction with maleic anhydride provided adduct (43) which was fully characterized. Apparently, the reactivity of compound (27) is so high that warming a solution of (27) to room temperature induced dimerization.

The chemical shifts of tri-*tert*-butyl[4]annulene (27) are shown below:



Pople-Untch equation:

$$1 = -(\pi^2 e^2 \beta_0 / h^2 c) S(32\lambda^3 M^2) x$$

$$\sum_j^{\text{occ}} [1 + 2\lambda \cos(4\pi j/M) + \lambda^2]^{-3}$$

$$[\lambda + (1 + \lambda^2) x \cos(4\pi j/M) + \lambda \cos^2(4\pi j/M)]$$

i.r. at 4 K argon matrix

No band between $1700\text{--}1490\text{ cm}^{-1}$

Figure 23

Using the C(2) proton (δ 6.40) of cyclopentadiene as a reference, $\Delta\delta = 1.04$ may be interpreted as being due to a paramagnetic contribution by the induced ring current in this compound. Using several assumptions, in particular, the rectangular geometry predicted for [4]annulene by Dewar, the Pople-Untch equation gives a paramagnetic contribution of 1.18 p.p.m. for the system. The agreement between the experimental and calculated values is excellent, but is subject to the arbitrary choice of the reference compound. The infra-red spectrum of this compound in an argon matrix taken at 4 K shows no absorption between $1700\text{--}1490\text{ cm}^{-1}$, indicating that the system at least does not exhibit a normal double bond absorption. The infra-red spectrum of the system will be discussed later. Now, the central and most crucial issue of the [4]annulene system concerns its

geometry. The result of the x-ray crystallographic analysis¹⁵ of (28) is shown below.

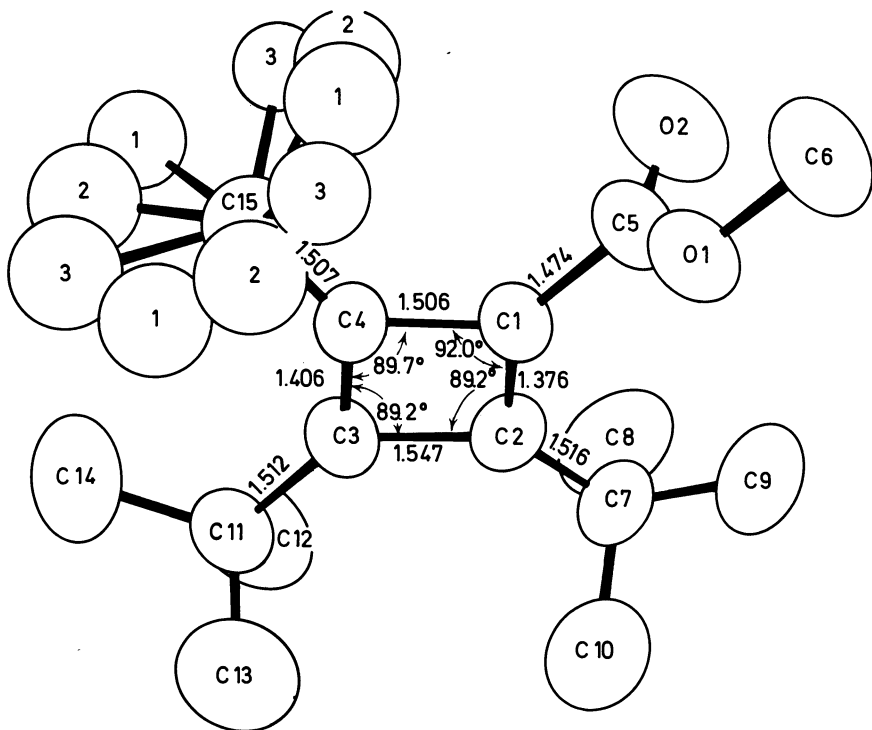


Figure 24

This is the first crystallographic analysis performed on a [4]annulene derivative which is perturbed mainly inductively by substituents. The π -system of the methoxycarbonyl group is orthogonal to that of the ring system. It is remarkable to see that the system is definitely not square but a slightly distorted rectangle. Because of the free rotation of one *tert*-butyl group, the R factor at present is 0.105, the error in bond length thus being ± 0.005 Å and that in bond angle being $\pm 0.3^\circ$. The relative occupancies of this rotating *tert*-butyl group are 51, 32 and 17 per cent. Further refinement by a hindered rotor model is currently in progress. The two short bonds C(1)—C(2) and C(3)—C(4) are 1.376 and 1.406 Å respectively and are within 3σ of the accepted aromatic bond length of 1.395 Å, and are definitely much longer than normal double bonds (1.334 Å). Of the longer bonds, only C(2)—C(3) is of single bond character whereas C(1)—C(4) has a length similar to that between C_{sp^2} and C_{sp^3} . The inequality of the two shorter bonds or of the two longer bonds is undoubtedly due to the presence of the bulky substituents.

SOME ASPECTS OF STRAINED SYSTEMS

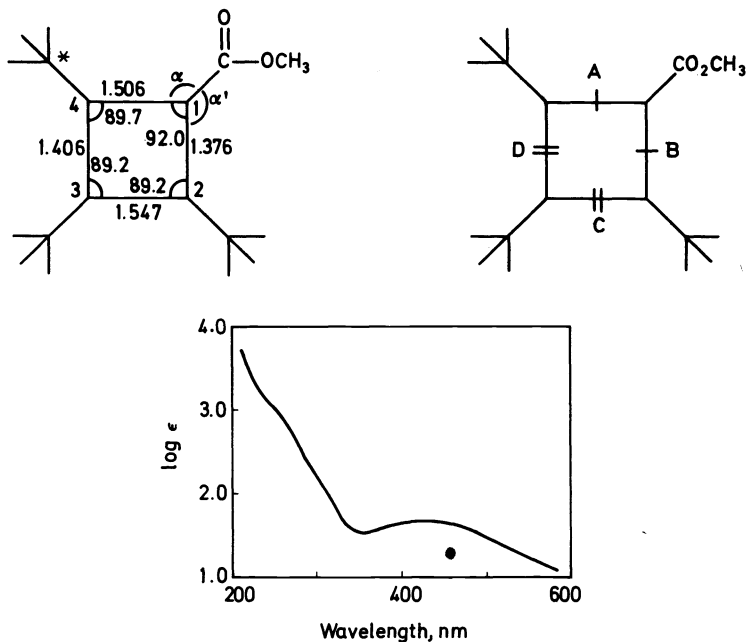


Figure 25

Even though there appears to be overcrowding of the *tert*-butyl groups, the closest H—H approach in this conformation is 2.13 Å, which is not significantly shorter than the van der Waals contact of 2.2–2.3 Å expected for hydrogen atoms.

The four carbon atoms of the ring are strictly coplanar. Also the four atoms of the methoxycarbonyl group are in a plane. The dihedral angle between the plane of this group and that of the ring is 84.1°. Steric interactions with the neighbouring *tert*-butyl groups clearly impose this conformation on the C(1)—C(5) bonds, thus little or no π -electron overlap from the methoxycarbonyl with the ring is possible. Because of the equality of the exocyclic angles, α and α' , neighbouring interactions of the methoxycarbonyl groups with the *tert*-butyl groups on C(2) and C(4) are not severe and appear to be of the same order of magnitude.

Since the π -system of the ring is orthogonal to that of the methoxycarbonyl group, one can assume that all the substituents on the ring exert largely inductive effects, thus the evaluation of the ultra-violet spectrum of this derivative in terms of the electronic state of [4]annulene is valid. One observes only weak, forbidden transitions above 300 nm ($\epsilon < 100$) and strong, allowed transitions near 200 nm. This is in agreement with Allinger's confident prediction^{10c} that [4]annulene has a singlet ground state.

Because of the substitution pattern of the compound, the two bonds C(1)—C(4) and C(1)—C(2) would be of equal length, if a square conformer

were at the true energy minimum of the system. Thus, the above crystallographic analysis is the first clear, direct evidence to demonstrate that a rectangle, distorted slightly by the substituents corresponds to the most stable conformation of the [4]annulene system (perturbed mainly by inductive effects). Thus, as far as this derivative is concerned, we have now completely defined the ground state: (i) *its geometry is near-rectangular* and, (ii) *its spin state is clearly singlet*. There are no observed e.s.r. signals, but the n.m.r. lines are sharp and allowed ultra-violet transitions appear only near 200 nm. The n.m.r. spectrum also shows there is an induced paramagnetic ring current in the ring system.

The problem now is centred around the ground state of the parent compound (2). Since Pettit first reported the generation of (2) in 1965¹⁶, there have been numerous experiments performed to define the properties of this elusive species. The list shown below is by no means complete and only briefly outlines the recent developments.

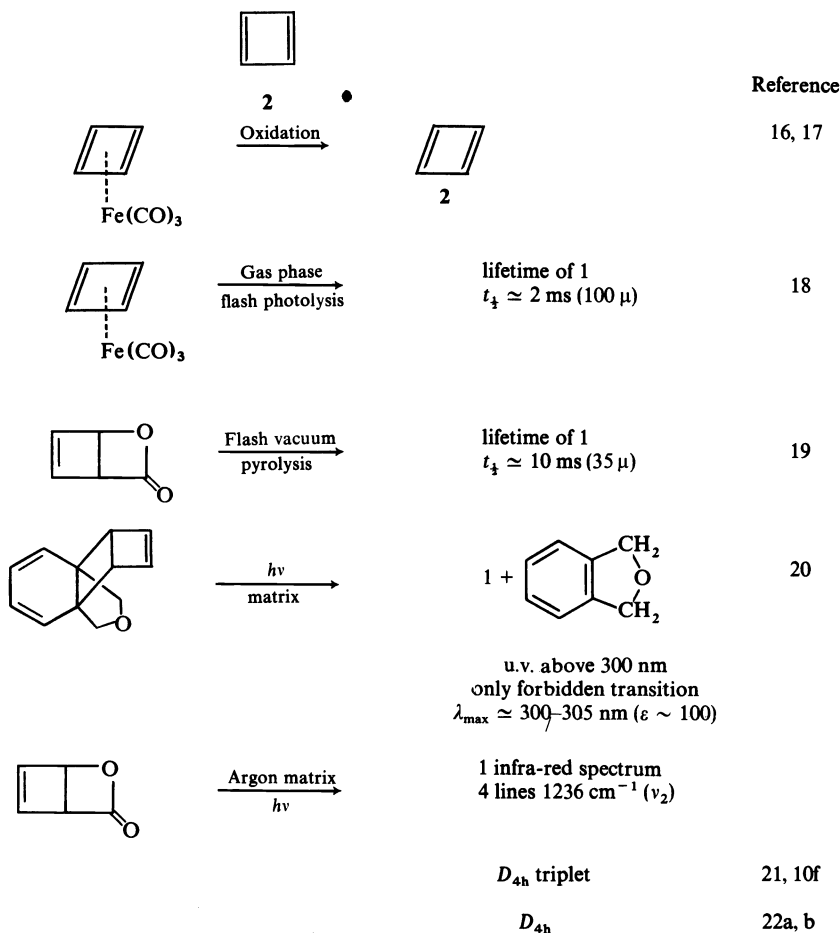


Figure 26

SOME ASPECTS OF STRAINED SYSTEMS

The original claim of Pettit has received support by the ingenious experiments, using an optically active [4]annulene iron tricarbonyl derivative, which were performed by Grubbs and Grey¹⁷. Using gas phase flash photolysis, we determined the approximate lifetime of (2) to be 2 ms at a pressure 100 μ ¹⁸. In the following year Hedaya and co-workers¹⁹ performed a flash-vacuum pyrolysis and concluded that the halflife is approximately 10 ms at 35 μ , in agreement with our previous findings. In 1972, the ultraviolet spectrum of (2) was measured and no strong absorptions were observed above 300 nm; only forbidden transitions appeared around 300 nm²⁰. In the same²¹ and following^{10f,22} years, (2) was detained in an argon matrix and its infra-red spectrum measured. The observation of only four lines, including one at 1236 cm^{-1} assigned to the ν_2 mode of skeletal vibration, and an analysis of line positions led Kranz, Lin and Newton^{10f} to conclude that the geometry of (2) is D_{4h} and its spin state is triplet. Chapman, McIntosh

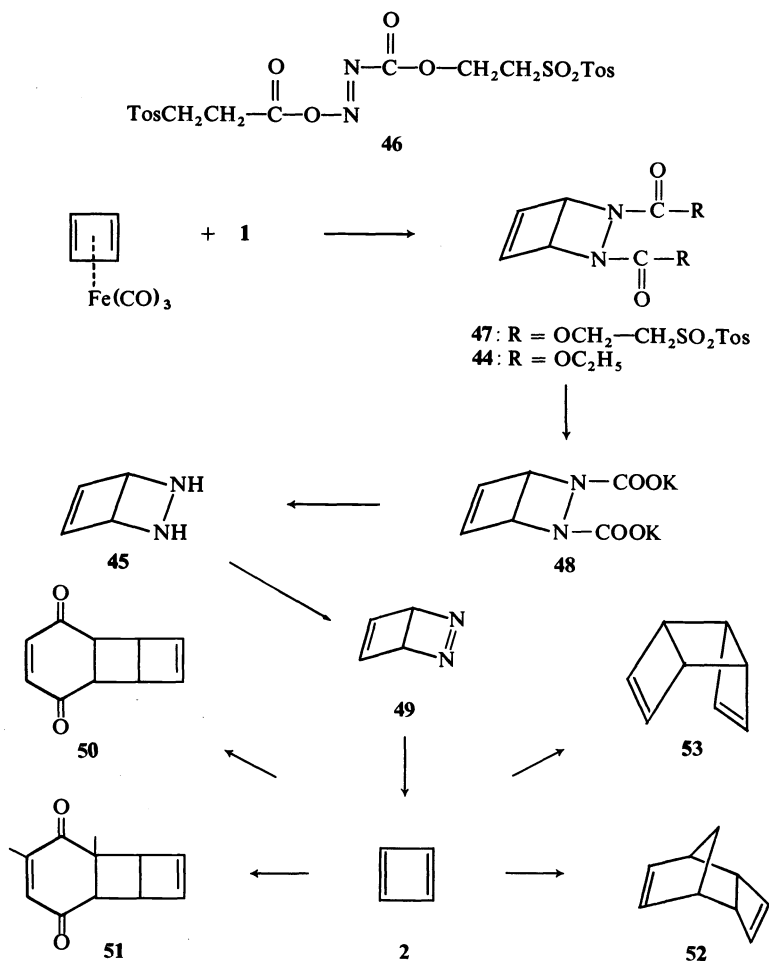


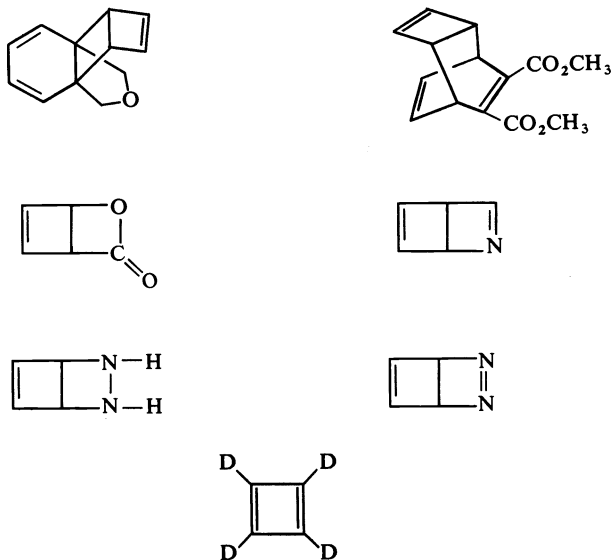
Figure 27

and Pacansky²² reported nearly the same result and made a 'tentative' conclusion in favour of the D_{4h} structure for (2).

There are a number of precursors of [4]annulene available now. The foregoing scheme shows one which we have prepared recently.

The dimethoxycarbonyl derivative (44) of a dihydrodiaz Dewar benzene, (45), has long been known, but removal of the methoxycarbonyl groups to obtain (45) has failed due to the sensitivity of the system. By the use of a new reagent (46), we have succeeded in obtaining (45), as outlined above²³. Oxidation of [4]annulene iron tricarbonyl in the presence of (46) provided the corresponding adduct (47), which in turn was hydrolysed under mild conditions to give (48). Upon acidification of (48), compound (45) was obtained. We have found that mild oxidation of (45) leads to diaza Dewar benzene (49), which spontaneously loses nitrogen to give (2). Compound (2) generated in this way was trapping in the usual manner, to afford (50), (51) and (52). In the absence of trapping reagents, (49) yielded the syn-dimer (53) of (2) as the sole product.

Listed below are some useful or potential precursors of [4]annulene.



54

Figure 28

Repeated attempts to observe e.s.r. signals that may be ascribed to a triplet ground state have consistently failed. In these experiments, (2) was generated under a variety of conditions such as a 4 K argon matrix, a 90 K organic matrix, and also from different precursors. We are now almost convinced that the ground state of (2) is singlet. Although we cannot present the *accurate* ultra-violet spectrum in its entire range at the present time,

there are definitely no intense absorptions above 300 nm. I wish to defer comments on the infra-red spectra which have been reported until we have completed our own experiments with fully deuterated [4]annulene (54). We also have some reservation in extrapolating the x-ray results of methyl *tert*-butyl[4]annulenecarboxylate to the parent compound, but we can at least summarize the current state of [4]annulene chemistry as follows: (i) the ground state is definitely singlet and, (ii) should D_{4h} turn out to be the true energy minimum then both D_{4h} and D_{2h} must reside in a region of a flat potential energy surface. However, it is more likely that the D_{2h} with two short bonds of approximately 1.37 Å, and the two long ones of the order of 1.51 Å would be the more stable ground state conformer. Cyclobutadiene is cyclobutaDIENE!

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Note added in proof: In the evaluation of the electronic structure of **28** presented in the text, the interaction of a Walsh type orbital of **2** with the π electrons of the methoxycarbonyl group has been ignored. The significance of this interaction remains to be examined.