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CYCLOBUTADIENE

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CONTENTS

1. INTRODUCTION

There are few molecules with a history comparable to that of cyclobutadiene.[a] Over the past century[1] this elusive species has continuously attracted the interest of both experimental and theoretical chemists, and recent intense efforts are particularly noteworthy. Accumulated evidence has now led to a mutually consistent conclusion as to several fundamental properties of CB in its ground state, which warrants a brief pause before further exploration of this challenging area is resumed. In this sense the present review is not intended to set a period, but rather a comma in the cyclobutadiene history. It includes an outline of the strategies followed in our and other laboratories, mainly designed to secure evidence pertinent to the ground-state geometry and multiplicity of CB, strategies which eventually proved to be successful. Also included is a critical evaluation of the recent theoretical developments in this area in order to emphasize the interrelation between experiment and theory. This account is concluded with a section dealing with possible future developments, outlining some remaining questions and also presenting suggestions as to what type of experiments might yield satisfactory answers to them.

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*The authors wish to dedicate this article to Prof. Tetsuo Nozoe on the occasion of his 77th birthday.
[a] Hereafter often abbreviated as CB.

Reference has to be rendered to Maier's excellent review[2] on CB which appeared five years ago. Although his main emphasis was somewhat different from ours, and this article concentrates on more recent achievements, minimal overlap is unavoidable when it is necessary to show how recent studies complemented or contradicted earlier ones. The reader is urged to resort to Maier's review especially for a full account of his own important contributions in the field.

1.1 *Background*

Perhaps it is appropriate to summarize the experimental and theoretical *status quo* pertaining to the cyclobutadiene problem at the beginning of the 1970s when we initiated our project.

1.1.1 *Theory.* It was early recognized that CB presented a unique problem in quantum chemistry and that it was not properly tractable within a one-electron MO or a simple VB approximation. Various qualitative and semi-quantitative arguments had been advanced from time to time, and those which appeared before 1967 are well summarized and critically discussed by Simmons and Anastassiou in Cava's classical book.[3] With regard to the geometry and multiplicity of ground-state CB in different conformations, three main possibilities had emerged from this discussion. These are visualized in diagrams A, B and C of Fig. 1(b) which depict a section through the C_4H_4-hypersurface along a (hypothetical) reaction coordinate q interconnecting two identical rectangular forms of CB via a square (Fig. 1(a)).

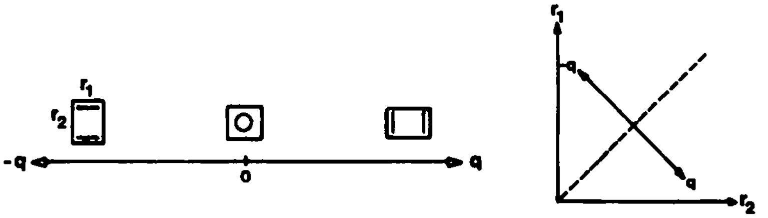

Fig. 1(a). Definition of a (hypothetical) reaction coordinate linking the two rectangular forms of CB.

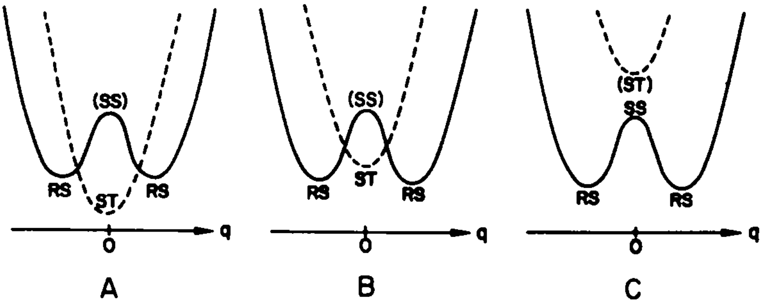

Fig. 1(b). Possible potential surfaces for the interconversion of two rectangular forms of CB. Designation RS: Rectangular Singlet, SS: Square Singlet and ST: Square Triplet. Abbreviations without brackets refer to the ground state, those in brackets to excited states.

Virtually all calculations agreed with the qualitative expectation (see Section 3.1.1) that CB in its lowest singlet state should possess a rectangular equilibrium geometry. In contrast, the relative energy of the lowest singlet and triplet state at *square* geometries was an issue of continued controversy. While various SCF methods predicted ST to lie below SS, and in one case[4] even below RS (possibility A), more elaborate CI-calculations[5] favored the inverse ordering. Some computations using single-determinant semiempirical methods were also performed and SS was predicted to lie 14.4 kcal/mole above ST[b] which in turn was 2.0 kcal/mole above RS (potential surface B).[6]

In 1967 Buenker and Peyerimhoff performed a comprehensive state-of-the-art *ab initio* study on CB.[7] They evaluated the effect of full π-space CI at four different geometries including those representing the

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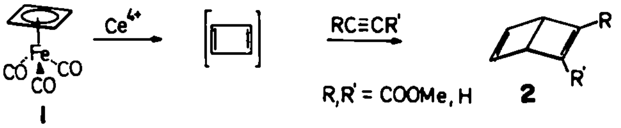
[b] Note that SS and ST are actually required to be degenerate within the Zero Differential Overlap (ZDO) approximation on which these procedures are based. This apparent contradiction will be discussed in Section 3.2.2.

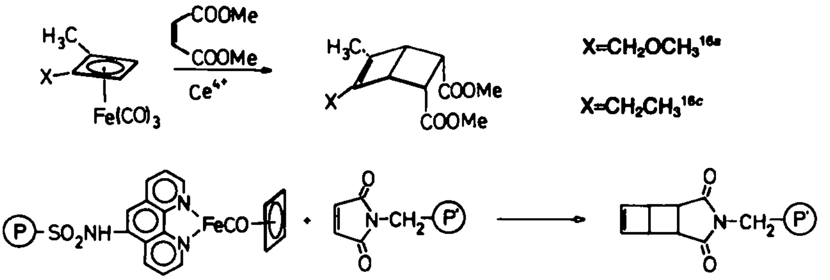
minima for singlet and triplet CB obtained by Dewar *et al.* with a semiempirical π-procedure.[8] RS was indeed predicted to be the ground state of CB and the lowest triplet state was higher in energy than the singlet state at all geometries considered (case C in Fig. 1(b)). Allinger's PPP–CI calculations on CB performed at almost the same time[4,9] concluded that, if singly *and* doubly excited configurations were included in the CI-part, the order of stabilities was in full agreement with that of Buenker and Peyerimhoff. The calculation on the electronic spectrum of CB showed that, while RS had no allowed transitions above 200 nm (with two forbidden ones above 450 nm), ST was to exhibit a fairly strong band ($f = 0.2$) around 370 nm. This information later proved to be extremely useful to experimentalists.

1.1.2 *Experimental.* By 1967 a wealth of experimental work on CB and its derivatives had accumulated, enough to cover an entire book.[3] However, virtually no information directly related to the properties of the parent system was available.[c] Cava wrote, "The little that is known about the chemistry of cyclobutadienes indicates that they can react as triplet diradicals".[3] This view was, however, soon challenged by Pettit. His brilliant synthesis of CB-irontricarbonyl[13] and subsequent investigations led to renewed interest in the parent compound. The oxidative removal of the metal from the complex 1 with the Ce(IV) in the presence of a dienophile led to the formation of the $2_\pi + 4_\pi$ adduct, as shown below, and this result indicated that the generation of free CB might have been achieved as a transient species in the reaction.[14]



Scheme 1.

Subsequently, Pettit provided evidence to support this view with a series of experiments designed to show that the iron carbonyl was not involved at the time when the cycloaddition reaction on CB took place.[15] The final proof for the existence of free CB under these conditions was given later (in 1972 and 1975) by three groups, two of them employing an optically active derivative of 1[16] and the other utilizing 1 and the dienophile supported on different polymers (three-phase test).[17]



Scheme 2.

In the trapping experiments CB reacted in a *stereospecific* manner both as a diene[14,18,19] and as a dienophile.[18,20] While this result does not necessarily prove that the reactions always take place in a concerted synchronous manner,[d] it likely rules out the intermediacy of triplet biradicaloid species in these reactions. Pettit also found that the species generated from dihalocyclobutenes with zinc dust[22] underwent similar reactions and concluded that this synthetic method proposed earlier by Nenitzescu[23] indeed provided CB.

In contrast with the above behavior, however, CB generated by pyrolysis of a photo-α-pyrone (see Section 2.2.2) at 800° could readily be "titrated" with allyl-, methyl-, and iodo-radicals as well as with oxygen,[24] reactions characteristic of diradicals and not usually observed in normal polyenes. Also this pyrolytic procedure permitted the measurement of the half-life of CB in the gas phase which was shown to be 10 ms at 35 mTorr, in reasonable agreement with another value (2 ms at 100 mTorr) obtained in a

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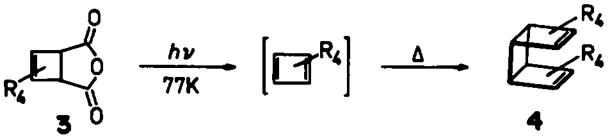
[c] It was known that the CB carbon framework assumes an equilateral geometry in transition metal complexes.[10] However, this is due to the severe orbital interaction between the central atom and the CB ligand[11] which results in the well known "aromatic" chemical behavior of the latter.[12] Thus, obviously, no conclusions regarding free CB can be drawn from this result.

[d] In fact the reaction of 1,3-di-t-butyl CB with TCNE does not give the normal Diels–Alder adduct but instead a 1,3-bridged bicyclobutane derivative.[15] Although this outcome can in principle be explained in terms of a concerted 2+2+2 cycloaddition,[15] it would be more straightforward to assume the intermediacy of a zwitterionic species as observed in other special cases.[21]

different manner[25].[e] Meanwhile, Maier and his group had undertaken a number of photolytic studies of partially or fully alkylated cyclobutadicarboxylic acid anhydrides (3)[28–31] and the appearance of UV absorptions upon irradiation of 3 in organic matrices at low temperature was taken as evidence for the successful generation of the corresponding CB derivatives. Upon warming the photolysates, they could only recover the dimers 4 of these compounds (along with other reaction products). Hence, the methyl groups appeared not to be bulky enough to permit the isolation of such CB derivatives in monomeric form. These and subsequent extensive studies performed in the 1970s by Maier's group are summarized in the review article[2] mentioned earlier.



R_4 = various combinations of H, CH_3 and $C(CH_3)_3$

Scheme 3.

Thus at the end of the 1960s the chemistry of cyclobutadiene was somewhat confusing, but the time appeared to be ripe for a next leap in our understanding of this elusive species. The available information at least hinted at the direction of further investigation, and experimental techniques required to solve some of the important problems were already available.

1.2 *Synthetic strategy*

The experiments summarized above demonstrate clearly that cyclobutadiene undergoes dimerization and other intermolecular reactions with extraordinary ease; nonetheless, it is apparently stable with respect to decomposition or rearrangement. The realization of this simple fact immediately suggested the following two approaches for the elucidation of the important ground-state properties of the system:

(a) The synthesis of derivatives which are substituted highly enough to block dimerization. This would permit their characterization, hopefully including X-ray analysis. However, the substituents should be chosen in such a way that the π-system of CB is only minimally perturbed.

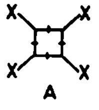
(b) The photochemical generation of a simply substituted CB or the parent compound in a noble gas matrix at cryogenic temperature. If the dimerization of the generated species is suppressed under these conditions, then ESR (spin state), UV (electronic structure), and IR spectroscopy should provide valuable information. Due to its small size and probably high symmetry, CB would very likely be amenable to complete vibrational analysis. Thus IR promised to provide the most direct insight into the ground state geometry of this molecule.

These two approaches provide mutually complementary information and indeed both of them have been pursued in recent years. For the sake of convenience and clarity, the chemistry of CB derivatives and then the parent species will be presented separately in the following sections.

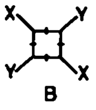
2. RECENT EXPERIMENTAL DEVELOPMENTS

2.1 *Derivatives*

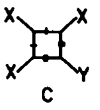
Pursuing a strategy as mentioned under (a), one must bear in mind the following point: The protective substituents must be arranged around the central ring in such a fashion that they do not impose a bias toward a rectangular geometry.[32] This requirement is fulfilled if all four bonds are formally equivalent as in derivatives of type **A** and **B**, and also if *adjacent* bonds are pairwise equivalent as in **C**. Although different substituents may still induce a rhombic (**B**) or kite-shaped (**C**) distortion, a strong alternation of bond lengths in the central ring would always reflect a property inherent to CB. Note that this is not necessarily true in derivatives of type **D**.



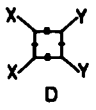
A



B



C



D

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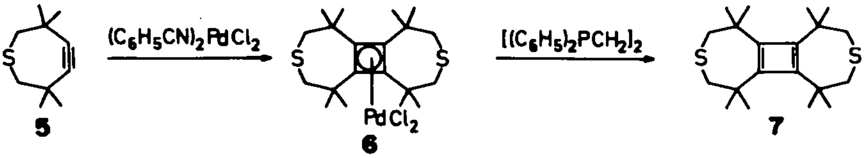
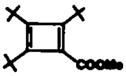
[e] In 1969 Li and McGee claimed to have condensed CB together with byproducts of pyrolysis of 1 at −196°, because subsequent warmup to −105° provided a species with m/e 52 (AP = 9.55 eV).[26] This species was, however, later identified as vinylacetylene.[27]

Before we elaborate upon our own work, Kimling and Krebs' brilliant experiments which appeared in 1972 at the initial stage of our project must be mentioned. Complexation of Pd(II) with the strained acetylene **5** provided the CB-complex **6**, which upon ligand exchange provided the first isolable, crystalline derivative **7**,[33] the first demonstration that CB can indeed be "protected" with bulky substituents. While this derivative provided valuable information, the pattern of the substituents does not meet the criteria described above. The presence of the two S-containing 7-membered rings creates different environments for adjacent bonds of the ring system, thus placing **7** in the category D.

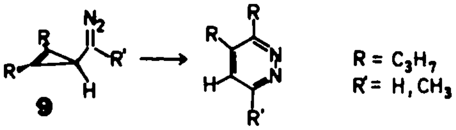


Scheme 4.

2.1.1 *Methyl tri-t-butylcyclobutadienecarboxylate.* In the light of the above consideration, tri-t-butyl-CB-carboxylate **8** was chosen as our first synthetic target. The well-known ring expansion method of cyclopropylmethylenes which are usually generated from the corresponding diazo-compounds either photochemically or thermally was serendipitously found to proceed in excellent yield with highly substituted diazo-precursors.[34] This success is partly due to the fact that the rearrangement to pyridazines as observed for **9**[35] is suppressed by the steric bulk imposed by the t-butyl groups.

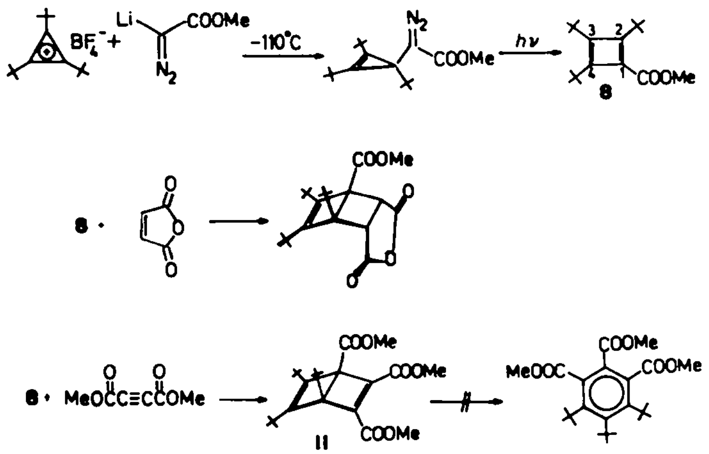


8



Scheme 5.

Scheme 6 summarizes the synthetic route to **8**. This derivative was highly reactive toward oxygen and reacted with maleic anhydride and acetylenedicarboxylate to form Diels–Alder adducts **10** and **11**, respectively[34] (note that **11** did not rearrange to the aromatic isomer due to steric hindrance).



Scheme 6.

The ^{1}H NMR spectrum of **8** displays three signals at $\delta = 1.13$ ppm (18H) [only one signal for the two t-butyl groups at (C(2) and C(4)], 1.19 ppm (9H) and 3.42 ppm (3H), indicating either that the ring system of **8** contains pairwise equivalent adjacent bonds [C(1)–C(2) = C(1)–C(4)] or that two rectangular forms are rapidly interconverting. Compound **8** shows no allowed electronic transitions above 250 nm, but a weak, broad band with a maximum at 425 nm, a UV/VIS spectrum in accord with Allinger's predictions for RS-CB.[4,9] The photoelectron spectrum exhibits a very low ionization potential $I_{p,1} = 6.9$ eV.[36]

Most importantly, an X-ray analysis performed on a single crystal of **8** reveals that the central ring framework is completely planar and clearly displays *localized* double bonds.[37] The perfectly normal thermal ellipsoids indicate that the bond-switching process observed in solution is completely blocked in the crystalline lattice.

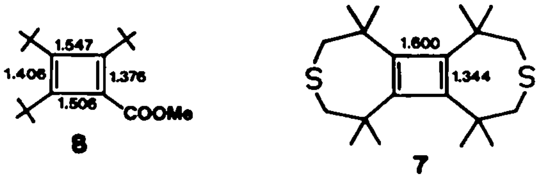


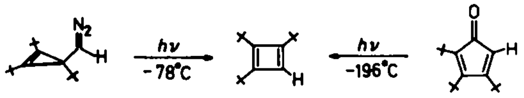
Fig. 2. Structure of two stable CB-derivatives.

Thus it was not astonishing that the X-ray analysis of **7**[38] also revealed similar features, although the alternation of bond lengths was even more pronounced as would be expected for a D-type derivative.

The question remained whether any of the substituents in **8** might have caused a significant perturbation of the π-system. The plane containing the carbomethoxy group is found to be at an angle of 84° to the CB-ring, and the geometry assures minimal interaction with the π-system. As for the σ-system[f] there is no apparent reason to assume that the perturbation caused by the substituents induces the observed *rectangular* distortion. The observed geometry is therefore most straightforwardly interpreted to reflect the intrinsic nature of the CB system itself.

2.1.2 *Tri-t-butyl-cyclobutadiene.* Cyclobutadiene is a cyclic, fully conjugated polyene and belongs to a series of compounds grouped as annulenes. These compounds are subdivided into two classes, $(4n+2)\pi$- and $(4n)\pi$-electron systems, according to a variety of unusual properties they exhibit.[39] The paramagnetic ring current induced by an external magnetic field is often taken as evidence to show the "antiaromaticity" of the latter systems[40] (for a discussion of this feature, see Section 3.1.2), and thus the magnetic properties of CB, the smallest prototype of the $(4n)\pi$ series, are of great interest. In order to secure this information, we embarked upon the synthesis of tri-t-butyl-CB **12**[34] which would hopefully survive long enough to permit NMR-measurements prior to dimerization.

The instability of the diazo precursor precluded its purification, and therefore CB derivative **12** could only be obtained along with minor amounts of side products (mostly cyclobutene derivatives) in solution at −78°. Upon irradiation the pink color of the diazo compound **13** vanished and the ^{1}H NMR-spectrum started displaying a new resonance line at $\delta = 5.38$ ppm at the expense of the signal at 4.07 ppm assigned to the proton adjacent to the diazo group in **13**. The $\delta = 5.38$ signal as well as the bright-yellow color of the sample disappeared upon exposure to air or warming to room temperature.



Scheme 7.

This new product **12** readily reacted with dienophiles to give adducts similar to **10** and **11**. Simultaneously and independently, Maier and Alzerraca prepared compound **12** by photochemical decarbonylation of 2,3,4-tri-t-butylcyclopentadienone **14a** at 77K,[41] and the excellent agreement in the physical and chemical properties of the photoproducts from the two different sources further confirmed the assigned structure **12**. The ring proton of **12** actually appeared at a significantly higher field than, for example, the proton at C(2) in cyclopentadiene, an appropriate (but somewhat arbitrarily chosen) reference compound, void of the effects of ring currents. The shift difference amounts to 6.42-5.38 = 1.04 ppm. This effect is indeed opposite to the one in benzene [as compared to the C(3)-proton in cycloheptatriene; $\Delta\delta = 6.55–7.40 = -0.85$ ppm], thus confirming the presence of a paramagnetic ring current in the CB-ring similar to that observed earlier in the larger (4n)-homologs, 12- and 16 annulene.[40] To our satisfaction, $\Delta\delta$ obtained from a theoretically based formula for the calculation of ring currents in

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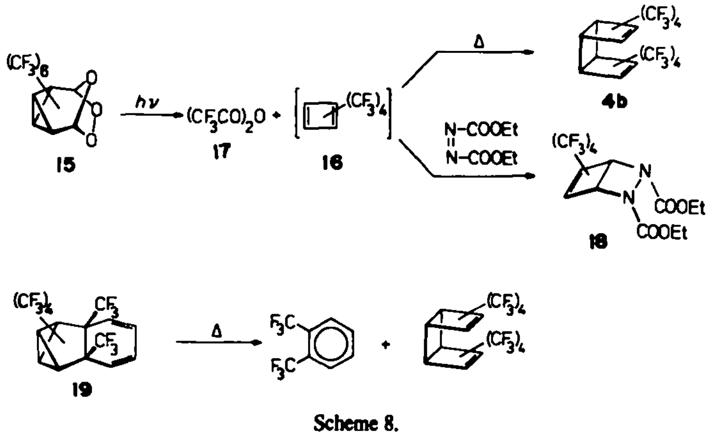
[f] CB possesses a high-lying Walsh orbital capable of interaction with π- and π^*-orbitals oriented parallel to the ring plane.

annulenes (Pople–Untch[42])[g] turns out to be 1.18 ppm in excellent agreement with experiment. Compound **12** which also exhibited only two resonances for the protons of the three t-butyl groups [$\delta = 1.05$ ppm (18H,s) and 1.12 ppm (9H,s)] was recently subjected to low-temperature NMR studies by Maier.[43] It was revealed that at −140° no broadening of the line at 1.05 ppm could be detected[41] and that a singlet assigned to the ^{13}C-resonances corresponding to C(2) and C(4) remained absolutely sharp even at −186°![43] This finding is very remarkable in view of the fact that **12** most probably possesses a nonsquare equilibrium geometry as well. According to Maier and Schweig this latter hypothesis found support through the photoelectron spectrum of **12**[44] which showed $I_{v,1} = 6.83$ eV, almost identical to $I_{v,1} = 6.90$ eV for **7**[45] and $I_{v,1} = 6.89$ eV for **8**.[36,h] If **12** had a square geometry, its $I_{v,1}$ would be significantly lower (by 0.7 eV according to CNDO/S calculations).[44] Thus, the low temperature NMR results can only be interpreted in terms of a very rapid bond shift as observed earlier for **8**.[34] Taking the chemical shift difference between carbon atoms 2 and 4 to be >1 ppm, this places an upper limit of 2.5 kcal/mole on $\Delta G^{\neq}$ of the bond-switching process.[43]

It should, however, be mentioned that this activation barrier is *expected* to decrease upon introduction of bulky substituents, since steric repulsion is minimized at square conformations. If the transition state would be rhombic rather than square (a possibility that cannot be ruled out *a priori* and is in fact required by certain group-theoretical arguments[46]), this effect would be even more pronounced (for a further discussion of this point see Section 3.1.1). Thus Maier's results should not be viewed as supportive of the claim that the parent compound might have an "effectively square" ground state geometry,[47–49] i.e. a very shallow potential surface for the interconversion of the two rectangular forms.

In addition to the above NMR studies, the chemistry of compound **12** has been extensively explored, and its multifaced, interesting behavior has been disclosed.[50,51]

2.1.3 *Tetrakis(trifluoromethyl)cyclobutadiene.* The studies on substituted CB's were thus far limited to C-type derivatives. In order to gain further information on CB, the investigation was extended to include four-fold symmetrically substituted (A-type) derivatives. Kobayashi *et al.* had made an interesting observation in experiments involving irradiation of ozonide **15** in organic glasses at 77K.[52] Upon thawing the matrix the photolysate provided white crystals which were shown by X-ray analysis to consist of the syn-dimer **4b** of tetrakis(trifluoromethyl)CB **16**.



Scheme 8.

When the photolysis was carried out in the presence of ethyl diazodicarboxylate, a very strong dienophile, adduct **18** was formed in high yields. These experiments suggested that monomeric **16** had indeed been formed as a primary product of photolysis. Dimer **4b** was also recovered as a major product after flash thermolysis of **19** at 500°/50 Torr, indicating the intermediacy of **16**[53].[i] Efforts to characterize the monomeric species were soon rewarded. Thus, photolysis of **15** at 77K yielded a yellow solution which exhibited only two signals in the ^{19}F NMR-spectrum at $\delta(CFCl_3) = 69.0$ and 78.7 ppm, the latter

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[g] See footnote 18 in[34] for the assumptions made with regard to some of the parameters occurring in the Pople–Untch formula.

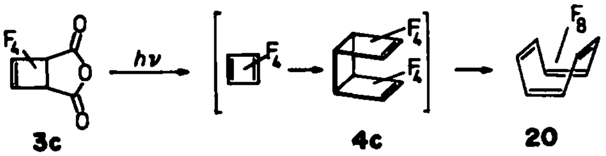
[h] In view of the differing central bond lengths **7** and **8** (and presumably also in **12**) this coincidence is probably due to the effect of the different substituents on the basis energies of the two double bonds, effects which happen to cancel the changes in interaction terms (using LCBO-parlance).

[i] It is interesting to note that on lowering the pressure to 1 mTorr (and raising the temperature to 700°) dimerization is largely suppressed and a monomeric $C_4(CF_3)_4$-compound emerges as the main product.[34] This species was, however, identified as tetrakis(trifluoromethyl)butatriene.

being attributable to the co-fragment **17**. Upon warming the signals of dimer **4b** appeared at the expense of the one at 69.0 ppm while that of **17** remained unchanged. The ^{13}C signal [$\delta(\mathrm{SiMe_4}) = 135.7$ ppm] assigned to the skeletal carbon nuclei excluded the possibility that the photo-product might be a tetrahedrane derivative instead of **16**.[55] The exclusive formation of relatively stable **16** ($t_{1/2}$ = several hours at 135K) and **17** from **15** warranted a measurement of UV and IR absorptions. The electronic spectrum showed a weak ($\epsilon \simeq 10$) broad band with $\lambda_{max} = 370$ nm consistent with the observations reported for other CB derivatives.[34] The IR spectrum of the photolysate featured a number of bands clearly not belonging to **15**, **17**, or the solvent. Most notable among them is a modest absorption at around 1700 cm^{-1} reminiscent of the C═C stretching modes in similarly substituted cyclobutene derivatives. Thus all the evidence was in accord with a rectangular singlet species for **16**, the first symmetrically substituted CB derivative to be subjected to such extensive spectral characterization.

As far as the CB problem is concerned, we felt that all information obtainable from heavily substituted derivatives was now in our hands and that it was meaningless to put more effort into the synthesis of additional compounds of this type. No matter how ideal an isolable model compound would be, the result could be extrapolated to the parent molecule only with some reservation. Nonetheless, it must be mentioned that research involving substituted CBs has been carried further in recent years, and these compounds are described in the next section.

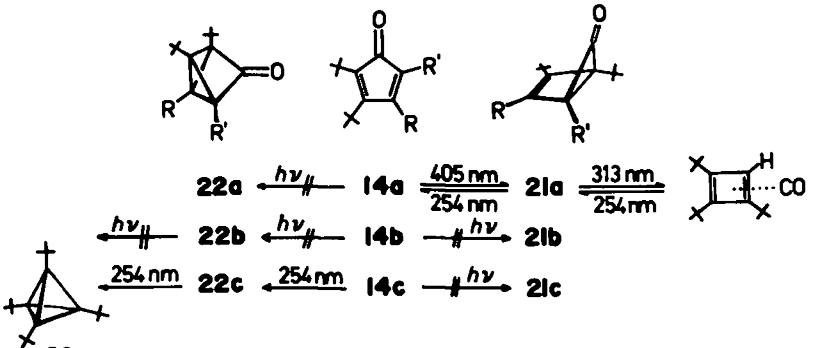
2.1.4 *Other derivatives*. Lemal advanced evidence for the intermediacy of tetrafluoro-CB generated by photolysis of anhydride **3c**:[56]



Scheme 9.

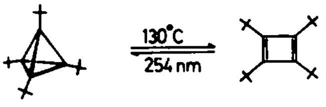
The only isolable product of his reaction sequence was, however, cyclooctatetraene derivative **20**.

More importantly, Maier's efforts directed toward the introduction of a fourth t-butyl group into the CB frame were recently rewarded in a very spectacular way.[57] He synthesized the fully substituted cyclopentadienone **14c** which fully lived up to the reputation of this family of compounds in showing a very peculiar and unpredictable photochemical behavior[2] as summarized in Scheme 10.



Scheme 10. Species a: R = t-butyl, R' = H
Species b: R = H, R' = t-butyl
Species c: R = R' = t-butyl.

Unlike **14b** which is photostable under all conditions,[41] **14a** can be transformed to housenone **21a**.[43] In contrast, this rearrangement cannot be induced in **14c** which in turn is converted to tricyclopentanone **22c** on irradiation at 254 nm.[57] Now we earlier prepared **22b** via a different route[58] and found that it was entirely photostable. Thus it seemed unlikely that **22c** would undergo photochemical decarbonylation. This inference turned out to be rash, as cleavage of **22c** surprisingly can be induced under appropriate conditions. To the great excitement of the chemical community, the primary product turned out to be the first derivative of long-sought tetrahedrane. Highly strained **23** rearranged to the originally sought CB derivative on warming to 130°.[57] Thus an isolable symmetrically substituted CB derivative has finally become available. Although its ring framework will certainly reflect the tendency of the four bulky groups to arrange themselves in an equidistant fashion, it would not be surprising if an X-ray analysis revealed a rectangular 4-membered ring.



Scheme 11.

2.2 *Parent compound*

Experimental evidence accumulated prior to 1972 clearly demonstrated that parent CB could not be studied as a monomeric species under normal conditions due to its extraordinarily high reactivity. The short lifetime of CB in the gas phase as well as in solution precluded the use of conventional spectroscopic methods. However, thanks to the pioneering work of Pimentel[59] and Porter,[60] the matrix isolation technique became available in the 1960s for the characterization of extremely reactive or unstable species detained in a suitable host material at low temperatures.[61] Thus, the photochemical generation of CB from an appropriate precursor in a matrix appeared to be the only viable alternative to tackle this problem.

2.2.1 *Selection of a suitable precursor.* The success of such experiments depends largely upon the selection of the photo-precursor which has to satisfy several requirements in order to serve as a useful source of CB under cryogenic conditions:[62]

(a) It should be volatile and/or stable enough to allow mixing with the host material in the gas phase without decomposition.

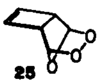
(b) It should have a UV (or visible) absorption in a wavelength range covered by one of the commonly available light sources and undergo cleavage with a high quantum yield and free from side reactions (long irradiation might destroy CB or damage the matrix through heating).

(c) The co-fragment(s) formed along with CB should not absorb at the wavelength of irradiation (internal filter effect), nor should it (they) interfere with the spectral observation of CB.

(d) The properties of "free" CB should not be severely altered through interaction with co-fragments (trapped within the same matrix cavity).

Screening various possible precursors, both (then) known and unknown, revealed that none fulfilled all of the above requirements simultaneously. The azo compound **24**, if deposited in a matrix, would serve as an ideal precursor (criteria b–d), but was soon found to be too thermolabile to permit appropriate handling.[63] A similar comment applied to ozonide **25** which, in addition, created problems in its synthesis, although its fully methylated derivative successfully provided tetramethyl-CB upon photolysis.[64] Compound **26** underwent photo-induced intramolecular cyclization concomitantly with the desired fragmentation[65] and this major side reaction excluded **26** from the list of candidates. Although the remaining two compounds **27**[66] and **3a**[2] met criteria a and c, their UV spectra (exhibiting virtually no absorption above 250 nm) suggested that photo-fragmentation of these compounds might proceed inefficiently[30] and CB might thus be photo-decomposed upon prolonged irradiation as it was formed. Furthermore, alkylated derivatives of **3a** were known to form cyclopentadienones concomitantly upon photolysis.[28–31,67,68] Despite these disadvantages, both compounds have eventually proved to be useful precursors of CB.

24



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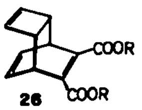

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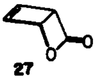

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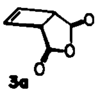
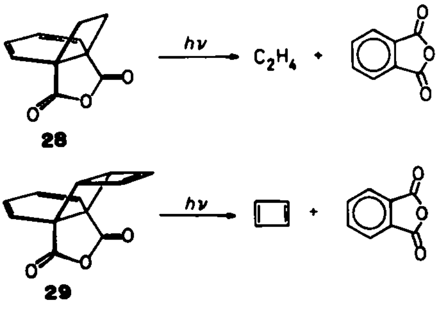


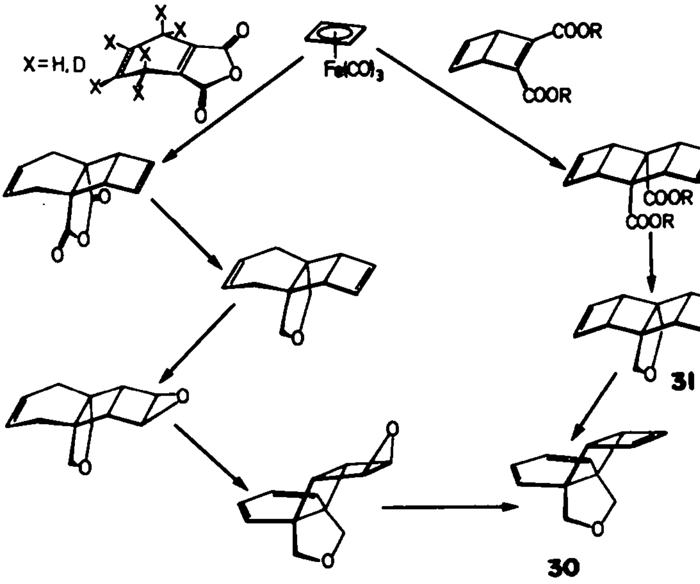
3a

It was known to us from other studies that compound **28** underwent efficient and quantitative



Scheme 12.

cleavage to yield phthalic anhydride and ethylene upon irradiation. It was therefore anticipated that triene **29** would undergo an analogous photo-fragmentation (see Scheme 12). However, since the co-fragment phthalic anhydride would mask the UV absorption of CB to a significant extent, the corresponding ether **30** was chosen as a photo-precursor. Two modified versions of the original scheme are available for the synthesis of **30**: one devised by Martin[69] involves thermolysis of the pentacyclic compound **31** and the other[58] is used to incorporate deuterium atoms in the cyclohexadiene moiety (see Section 2.2.3).



Scheme 13.

As expected, the ether **30** underwent efficient photo-cleavage, partly because of its intense absorption at 250–260 nm. First, the UV spectrum of the photolysate in degassed 2-methyltetrahydrofuran glass at −180° was recorded. The matrix was then thawed in order to effect dimerization of CB and the spectrum was recorded again after recooling to −180°. The difference of the two spectra is displayed in Fig. 3.[58,70] Since NMR and glc analysis of the photolysate after warming showed that the CB dimer **4** and phthalan are the sole identifiable products, the curve in Fig. 3 is believed to represent a section of the UV spectrum of CB.

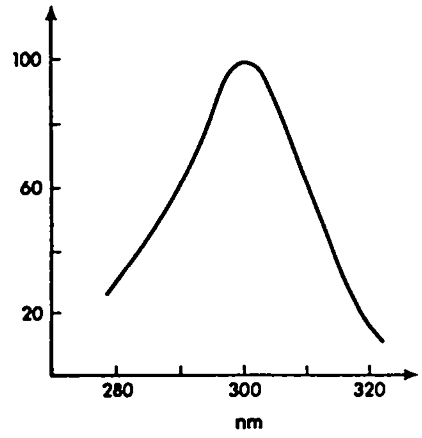
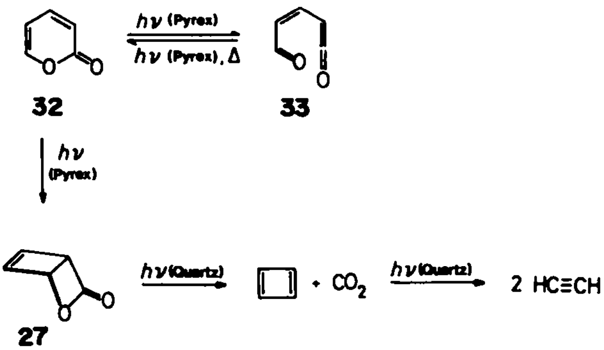


Fig. 3. UV-spectrum of CB (The absorptivities are based on total conversion of the starting material and should be regarded as approximate.)

2.2.2 *The IR problem.* The report on the above UV spectral identification of CB fell in the midst of two other communications announcing the first successful isolation and characterization of CB in matrices. The groups of both Chapman[71] and Krantz[72] simultaneosuly completed virtually the same preliminary IR spectral identification of CB.

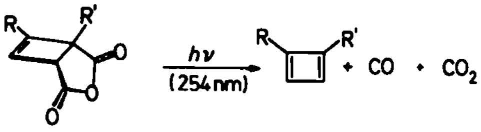
Chapman *et al.* found that the high sensitivity of photo-α-pyrone **27** required its generation *in situ* from α-pyrone **32**. But on irradiation through Pyrex the latter first underwent electrocyclic ring-opening to yield the earlier postulated aldehyde-ketene **33**,[73] until a near-photostationary state was reached.[74] However, irreversible intramolecular cyclization to **27** proceeding more slowly at the same time eventually depleted the sample of **32** to yield **27** as the sole ultimate product. Upon continuing the irradiation through quartz the photolysate started exhibiting three distinct, simultaneously growing IR absorptions, two strong ones at 570 and 1240 cm^{-1} and a somewhat weaker one at 650 cm^{-1}. Also noted was the gradual formation of acetylene as a result of photo-decomposition of CB, a stationary concentration of the latter being attained after a reasonable length of time. All three bands were assigned to CB. Chapman's evidence in favor of this assignment consisted in the observation that only these three bands vanished either on over-irradiation (giving acetylene) or careful annealing (allowing CB to dimerize), although not completely in the case of the 650 cm^{-1} band. His explanation for the latter feature was that a bending mode of CO_2 (which is observed at 660 cm^{-1}) was shifted somewhat due to its proximity to "secondary products" and now happened to arise at exactly the same wavelength where the CB band vanished.[71]



Scheme 14.

As group theory predicts four IR fundamentals for square C_4H_4 (one of them being a C–H stretching mode appearing as an extraordinarily weak absorption[71]), it was tentatively concluded that CB has a D_{4h} ground state geometry. In their first communication Lin and Krantz arrived at the same conclusion with regard to the bands to be attributed to CB (1236, 653 and 573 cm^{-1} in their report), although they refrained at that time from offering an interpretation of their finding in terms of the structure. Their additional claim that CB exhibited a weak, broad electronic absorption at 405 nm was later recalled by the senior author.[75]

Somewhat later than the above spectral identification of CB, Maier reported an extension of his earlier work on alkyl substituted CB derivatives.[76] His group employed different precursors, one of them being the anhydride **3a** which on prolonged irradiation with a low-pressure Hg-lamp was induced to provide CO, CO_2 and CB, albeit in low yields. According to Maier, the photolysate of **3a** at 8K displayed a weak UV-absorption with a peak at 301 nm. The same band was also observed upon photolysis of the more efficiently cleavable t-butyl-derivatives **3b** and **3c**. Amazingly, the concomitant formation of cyclopentadienones observed in many other alkylated derivatives of **3a**[28-31,67,68] was completely absent in the case of **3a** and **3b**. Before we discuss the implications of these results, two further publications that appeared shortly after those described above should be mentioned. Chapman extended his studies to include mono- and dideuterated derivatives of CB[77] and Krantz reported on his IR-measurements on the monodeuterated derivative.[78] Table 1 lists their results together with those of a force-constant cal-



3a: R=R'=H
3b: R=C(CH_3)$_3$, R'=H
3c; R=H, R'=C(CH_3)$_3$

Scheme 15.

culation[78] (*vide infra*) and the assignments of the absorptions to the modes of vibrations as favored by both authors.

Table 1. IR-frequencies observed for CB and its deuterated derivatives

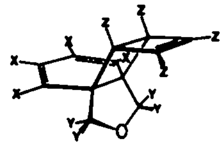
		Ring deformation			C-H-bend in plane			C-H-bend out of plane		
C_4H_4	(Chapman)		1240		650			570		
C_4H_4	(Krantz)		1236		653			573		
C_4H_4	(calc. D_{4h} Newton)		1236		661			576		
C_4H_3D	(Chapman)		1223	780	654			576	535	
C_4H_3D	(Krantz)		1224		653		594		540	460
$1,2\text{-}C_4H_2D_2$	(Chapman)	1212	1188	770	654		583	576		
$1,3\text{-}C_4H_2D_2$	(Chapman)	1216	1182	781	654	633	583	576	535	

While Chapman noted that the absence of two distinctive vicinally dideuteriated derivatives (1,2-and 1,4-d_2-CB) was consistent with his tentative conclusion that CB had D_{4h}-symmetry,[77] Krantz was now being considerably more explicit. His assignment was based largely on a normal coordinate calculation he and Newton had performed on the D_{4h} species and a trial set of force constants reproduced the band positions almost to the wavenumber. Using the same force field they calculated the splittings of the three degenerate modes upon descent to C_{2v} symmetry and again brought these results into accord with their experimental findings. They concluded that the appearance of the spectrum of C_4H_3D (differing significantly from Chapman's) and their calculations "solidly supported the assignment of the 1236 cm^{-1} and the 653 cm^{-1} band to degenerate modes of square cyclobutadiene".[78]

Although at that time none of the results on rectangular CB derivatives[38,39] mentioned in the previous section were available, it must be realized that this conclusion was in marked contrast to the image of CB as it had emerged from theoretical and chemical studies. (see Section 1.1; the ground state of CB was thought to be a rectangular singlet. A square equilibrium geometry would require CB to have a triplet ground state.) Krantz and Newton apparently realized this dilemma caused by their interpretation of the facts and thus considered the possibility of two very rapidly interconverting rectangles (an "effectively square" singlet).[78] Therefore, they performed some new calculations using the more flexible 4-31G basis set for HF-calculations on the SCF level and also the newly developed GVB program only to find that the results ruled out the possibility of an "effectively square" singlet structure. They emphasized the fact that both methods predicted a square equilibrium geometry for the triplet state but did not mention whether this minimum was higher or lower in energy than the rectangular singlet (see Fig. 1).

In view of this new situation an obvious step to take was to look for spectroscopic manifestations of alleged triplet CB. Thus we performed a series of ESR experiments on parent CB generated from different precursors under a variety of conditions (Xe or Ar matrices at 8K or organic glasses at 77K). None of these experiments revealed signals that could possibly be ascribable to triplet CB[37] in accord with Maier's earlier observations on methyl substituted CB.[31] In addition to this direct evidence against triplet CB, it should be recalled that PPP-calculations had predicted a strong transition at around 370 nm if CB were a square triplet.[4,9] While the spectra we[70] and Maier[2,76] reported do not agree very well with Allinger's predictions in terms of the precise position of the maximum of the weak absorption (*vide infra*), there was no doubt that *allowed* transitions ascribable to CB were *absent* above 250 nm, suggesting a singlet rather than a triplet ground state. Thus, a very intriguing explanation offered by Dewar[79,80] that CB may persevere for a prolonged period of time as a *metastable* triplet species at 8K was refuted immediately, since no significant changes occurred in the ESR, UV, and IR spectra (in a CH_2Cl_2 matrix) between 8 and ≈100K. Furthermore, the full characterization of several simple CB derivatives had been completed by this time and the rectangular singlet ground state for these compounds been firmly established.

These results led to a scrutiny of the experimental evidence in favor of square CB. As noted above, four IR-active fundamentals ($3E_u$, $1A_{2u}$) are predicted for D_{4h} CB, one of them being a C–H stretching mode expected to give rise to an IR band of only low intensity. Descent to D_{2h} leads to a splitting of the three degenerate modes, increasing the number of IR-active fundamentals to seven, of which two are again C–H stretching modes. Thus CB will display *three* bands below 2000 cm^{-1} if it is square, and *five* if it is rectangular. Since the extra two bands could well appear with low intensity, it was easily conceivable that they had escaped detection in the earlier experiments. Thus we initiated reinvestigation of the IR spectra of CB with two distinct objectives: a search for possibly missed low intensity bands and the proper assignment of each IR absorption. The selection of the triene-ether **30**, the most efficient precursor thus far known for the generation of CB, and also the use of an FT-interferometer greatly improved the overall quality of the spectra. Although the rather rich absorptions of the co-fragment, phthalan, masked several critical regions, the proper incorporation of deuterium atoms into the precursors **30** (Scheme 16) shifted these absorptions and the entire range of the IR spectrum 200–4000 cm^{-1} could be closely examined for the bands arising from the vibrations of CB. In addition, the fact that we had the spectra of both C_4H_4 and C_4D_4, greatly aided in the vibrational analysis of the system.

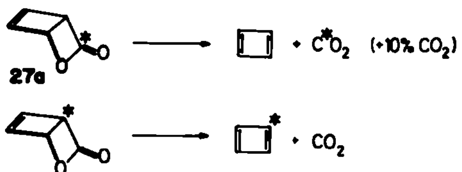


30

	X	Y	Z
30a	H	H	H
30b	H	D	H
30c	D	H	H
30d	D	D	H
30e	H	H	D
30f	H	D	D
30e	D	H	D
30f	D	D	D

Scheme 16.

It is rather ironic that in the first preliminary experiments we were observing *fewer* bands than Chapman and Krantz, instead of more: while the absorptions at 1240 and 570 cm^{-1} always emerged clearly upon photolysis and vanished upon annealing or overirradiation, we repeatedly failed to detect the reported band at 650 cm^{-1}.[81] Since earlier studies unambiguously showed that CB was indeed formed in our experiments, this latter band was obviously *not* due to CB! Maier independently made exactly the same observation[48] and reached the conclusion that the band at 650 cm^{-1} was due to a bending vibration of CO_2 shifted slightly from its usual position (660 cm^{-1}) as a consequence of its interaction with CB. In fact, a proof for this conclusion was offered later by Krantz.[75] He irradiated matrix-isolated precursors **27a** and **27b** containing 90 atom % ^{13}C in the positions indicated by the asterisks and found that the photolysate from **27a** contained *two* pairs of bands (636/644 and 655/662 cm^{-1}) with intensity ratios 9 : 1, while only the latter pair emerged on irradiation of **27b**. (Pure matrix-isolated CO_2 absorbs at 662 cm^{-1}.)

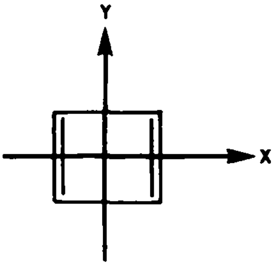


Scheme 17.

As the bands at 1236 and 573 cm^{-1} of CB remained unshifted in the case of **27a**, it was evident that CO_2 indeed displayed two bending modes that could arise either through a splitting of the degeneracy due to interaction with neighboring CB or from CO_2 molecules occupying different sites in the matrix. The above findings obviously did not solve the problem of D_{4h} CB, but instead revealed that the number of the observed bands lost its significance in the structural assignment of CB and that the argument in favor of D_{4h} rested solely on the assignment of the 1236 cm^{-1} band to the skeletal deformation mode of vibration,[75] the band position which happened to fall roughly in the middle of C–C and C=C bands.

2.2.3 *The solution of the IR problem.* Our investigations on **30a–h** during the following two years, which were mainly spent on solving a variety of technical problems, disclosed that there were in fact *four* different bands increasing in intensity upon irradiation and decreasing upon annealing, and their relative intensities remained constant throughout the photochemical and thermal processes. As anticipated, one of the new bands appeared with very low intensity while the other happened to be located very near to a group of absorptions due to acetylene that always formed as a secondary product in experiments with photo-α-pyrone. Table 2 lists the frequencies and relative intensities of CB and CB-d_4 obtained in a reproducible manner.[82]

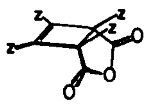
Table 2. Frequencies (cm^{-1}) and assignments† of vibrations observed for CB.



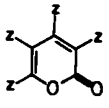
		C_4H_4	C_4D_4	Product Rule ratio[83] observed	Product Rule ratio[83] theoretical
B_{3u}	C=C stretch	1523	1456	-	1.927
B_{2u}	mixed C-C-stretch and C-H(D) bend	1240	1043	1.918	1.927
B_{2u}		723	609		
B_{1u}	C-H(D) wag out of plane	572	421	1.357	1.363

†In order to achieve consistency with the notation used by most spectroscopists and theoreticians, we exchanged the x- and z-axes relative to our previous choice.[82] The coordinate system depicted beside the Table is used consistently throughout our article.

We finally extended our investigations to include anhydrides **3a**, **d** and α-pyrones **32a**, **d**. Having known the new set of absorptions, we were able to detect all the lines listed in Table 2 (concertedly arising upon photolysis and decreasing upon annealing). These bands always appeared in pairs split by 1-3 cm^{-1} and shifted by 1-7 cm^{-1} with the exception of a larger shift and splitting in the 570 cm^{-1} band in the case of the precursor **3a**. The two different CO_2 absorptions at 660 and 650 cm^{-1} were also present both in the photolysate of **3a**, **d** and **32a**, **d**. This latter finding further confirmed the notion that some kind of interaction was taking place between CB and CO_2,[48] or CO[43] (but *not* phthalan[81,48]), although the effect was certainly small. Inspection of Table 2 immediately discloses several important features. The appearance of *four bands below* 2000 cm^{-1} leaves no doubts that the symmetry of CB is lower than D_{4h}. Although chemical intuition strongly suggests that the symmetry is D_{2h}, this inference cannot be drawn with certainty from the present limited information available from the IR spectral studies alone. The assignment of the 1240 cm^{-1} band to a framework deformation[75,78] is obviously doubtful judging from the large isotopic shift of 200 cm^{-1} and was indeed proved to be incorrect as shown below. While the band at 572 cm^{-1} clearly originates from an out-of-plane C–H bending, being shifted by 150 cm^{-1} upon deuteration, the 1523 cm^{-1} band is ascribable to a C=C stretching mode of vibration (isotopic shift, 67 cm^{-1}). Although the IR spectrum of CB cannot be interpreted in terms of group vibrations, it is worth noting that this latter frequency is not too far from normal cyclobutene C=C stretching frequencies. If we assume as a working hypothesis that CB has in fact D_{2h} symmetry, application of the product rule[83] allows us to assign the observed vibrations as shown in Table 2 where the irreducible representations correspond to a definition of the coordinate system as depicted beside the Table.



3a Z=H
3d Z=D



32a Z=H
32d Z=D

Apparently, we are left with an unobserved B_{3u} fundamental. Although there are some indications of very weak bands at ~1000 cm^{-1} in CB and ~750 cm^{-1} in CB-d_4, the present level of instrumental sophistication does not permit them to be unambiguously attributed to the missing vibrations.

In line with these assignments is the fact that a normal coordinate calculation[82] (assuming CB to have bond lengths of 1.37, 1.51 and 1.08 Å, respectively) converges to a reasonable set of force constants while reproducing the experimental spectra to ±17 cm^{-1}. However, the limited number of experimental data makes these results tentative and other combinations of geometrical parameters and force constants could possibly accommodate the IR spectra as well.

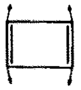
2.2.4 *Theoretical analysis of the IR spectra.* Although we shall deal with recent theoretical achievements in a separate section, we wish to first describe the results of quantum-chemical calculations dealing with the vibrational behavior of CB. The first of these by Dewar and Komornicki[80] involved computations of the normal vibrations for MINDO/3 geometry-optimized ST as well as RS-CB. Dewar viewed his results as supportive of a D_{4h} structure, because the calculated frequencies (576, 697 and 1085 cm^{-1}) were in reasonable agreement with the earlier experimental ones. However, a closer inspection of Table 8 in[80] reveals that the conformity is equally good for D_{2h} CB (see Table 3) and that all deviations remain fully within the usual range.

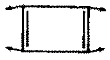
More recently two groups independently evaluated the force field of CB using *ab initio* SCF techniques. The more elaborate of these studies by Kollmer and Staemmler[84] used a very flexible basis set (double-ζ plus polarization functions) to optimize the geometry on the CEPA level (accounting for correlation effects) and then evaluated the force-constant matrix for the seven IR-active vibrations in a harmonic approximation on the SCF level. Their results are summarized in Table 3 along with those of Hess and Schaad[85] based on SCF calculations with an STO-4G basis set. The overall agreement with experiment does not deteriorate with the less flexible basis set, although it must be noted that the two studies were conducted at entirely different geometries. The averaged deviations are $-114\,\mathrm{cm}^{-1}$ for the double-ξ basis and $-101\,\mathrm{cm}^{-1}$ for STO-4G, the force constants being too high in all cases. Kollmar indicated, however, that better agreement is to be expected if correlation effects are taken into account on calculating the force constants as well.[84] A remarkable feature of these calculations is the clear demonstration that the intense $1240\,\mathrm{cm}^{-1}$ band was earlier misassigned to the skeletal deformation mode which should appear as an extremely weak absorption. In fact the calculated relative intensities of all bands are reproduced extremely well in experiment.

Table 3. Calculated frequencies (cm^{-1}) and relative intensities of IR-active vibrations in CB

C_4H_4	experimental	Kollmar & Staemmler	Hess & Schaad	Dewar
B_{3u} $\nu_{C=C}$	1523 (0.01)	1697 (0.02)	1769 (0.01)	1738
B_{3u} δ_{C-H}	1240 (0.41)	1377 (0.20)	1286 (0.70)	1211
B_{2u} ν_{C-C}	~1000 (~ 0)	1129 (0.00)	996 (0.01)	1007
B_{2u} δ_{C-H}	723 (0.12)	790 (0.05)	802 (0.04)	922
B_{1u} δ_{C-H}	572 (1.00)	692 (1.00)	638 (1.00)	645
C_4D_4				
B_{3u} $\nu_{C=C}$	1456 (0.03)	1612 (0.04)	1660	-
B_{3u} δ_{C-D}	1043 (0.21)	1161 (0.15)	1152	-
B_{2u} ν_{C-C}	~750 (~ 0)	823 (0.00)	718	-
B_{2u} δ_{C-D}	609 (0.16)	661 (0.11)	620	-
B_{1u} δ_{C-D}	421 (1.00)	508 (1.00)	468	-

In addition to the IR frequencies and intensities, Hess and Schaad also computed those for the Raman-active modes. A noteworthy result is that neither of the two skeletal A_g modes is well disposed to induce the bond-switching process, because the shortening of the C–C bond is only accompanied by a minor lengthening of the C=C bond along one of these normal coordinates ($R_{C-C} = -0.045$ Å and $R_{C=C} = +0.016$ Å at the classical turning points) and *vice versa* for the other one. Our normal coordinate analysis in fact has led to a similar prediction as the two skeletal A_g-vibrations A and B ("C=C stretching" and "C–C stretching") are virtually unmixed and the displacement of the nuclei takes place along lines that deviate only slightly from the C–C and C=C-axes, respectively.


A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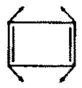

C

This feature has an interesting experimental implication. If, contrary to these predictions, the two modes turn out to be pronouncedly mixed (nuclear displacements more like those indicated in C corresponding to q in Fig. 1), i.e. the bond-switching process actually proceeds along a normal coordinate, this should manifest itself in a splitting of the corresponding Raman-band due to vibronic coupling (Fig. 4), thus possibly permitting an evaluation of the intervening energy barrier.

2.2.5 *The UV problem.* We have mentioned earlier that the UV-spectra of CB and its derivatives agree well in an important way with theoretical predictions for an RS ground state in that no strong absorptions were ever observed above 250 nm.

However, a minor but nonetheless disturbing discrepancy remains. The position and even the mere existence of a weak absorption is still being disputed in the case of parent CB and some of its simple derivatives.

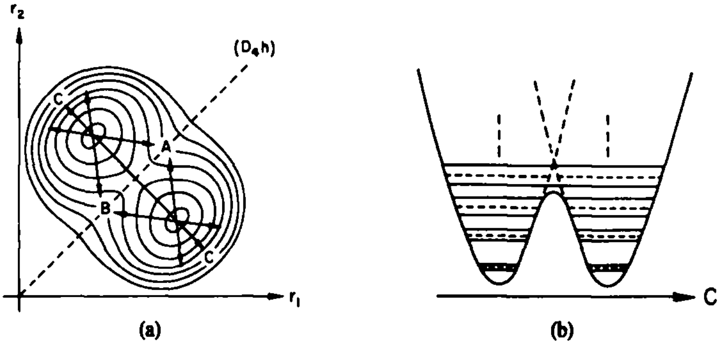


Fig. 4. (a) Two-dimensional hypersurface for the interconversion of the two rectangular forms of CB via a square. (b) Qualitative vibronic state diagram for Section C through the hypersurface depicted in 4(a).

Recall that all three CB derivatives isolated to date show faint but discernible bands around 425 nm[33,34,57] and two other CBs which are stable only in solution also absorb at 425[43] and 370 nm.[55] Thus, the (theoretically predicted) presence of an excited state of CB accessible through interaction with visible or near-UV photons has been experimentally confirmed beyond any reasonable doubt.

The corresponding transition is expected to show up even more weakly in the parent compound, and it might be considerably shifted relative to the above derivatives due to the large influence of inductive substituents on the highly polarizable π-system of CB. The search for absorption bands of non-isolable CBs has repeatedly been hampered through cogeneration of side-products obscuring parts of the spectral region of interest[31,67,68] or forming CT-complexes with CB and thus perturbing its electronic system.[49,67,86] After these difficulties were recognized[86] and ways to circumvent them had been designed, it was largely agreed upon that CB[70,76] (and t-butyl-CB[2,76]) shows a weak but discernible absorption maximum at 300–305 nm (see Fig. 3).

Recent experiments have yielded evidence that CB does not only interact with strong acceptor molecules but also with CO_2 and CO trapped within the same matrix cavity,[43] although the intermolecular forces are predicted to be very weak and presumably repulsive in this case.[87] These findings apparently induced Maier to revoke his earlier claim that the band at 300–305 nm was due to CB,[48] and he presently maintains the opinion that free CB shows no absorptions above 300 nm in contrast to our findings.

However, weak absorptions are very difficult to confirm in cryogenic matrix experiments and the band at 300 nm which we repeatedly reproduced, both at 8K and 77K in the photolysis of ether **30**, may well escape detection under somewhat different conditions than those employed in our laboratory. The importance of such considerations is underlined by the fact that tri-t-butyl-CB, which was earlier claimed to show "no well developed band above 300 nm",[41] was recently found to display maxima at 405 and 425 nm,[43] in accord with that reported for tetra-t-butyl-CB.[57] We believe that there is reason to maintain our claim that CB shows a faint but distinct absorption maximum at 300 nm (see Fig. 3) which definitely can not be explained in terms of a CB–CO_2 complex.

3. THEORETICAL PART

3.1 *General remarks*

Some comments on two terms often used in discussions of the CB problem appear to be in order before we present an in-depth analysis of recent quantum-chemical calculations on the CB system.

3.1.1 *The Jahn–Teller effect.* The first of these terms is "Jahn–Teller distortion". In a simple orbital description, used for example in Hückel theory, the two highest occupied orbitals of CB are degenerate and populated by two electrons. From the resulting degeneracy of the ground state in this treatment, it is often inferred that CB is subject to Jahn–Teller (JT) distortion. This notion, however, is not entirely correct. Although Jahn and Teller originally formulated their principle in terms of orbital degeneracy,[88] it only applies in cases where this degeneracy is also a property of the state in question and is not an artefact of the model used to describe it. The ground state of CB is a case where this distinction must be considered, as inclusion of electron repulsion causes a splitting of the degeneracy. Öpik and Pryce recognized in 1956 that species with narrowly spaced electronic states at highly symmetrical conformations may behave as if they were JT-active.[89] Thus the situation discussed by Jahn and Teller can be viewed as the limiting case of a special form of vibronic interaction generally operative in the case of near-degeneracy. Coulson first applied this reasoning to CB[90] and proposed that a "pseudo" JT-effect[j] was responsible for the rectangular distortion of the lowest singlet state.[k]

Apparently, the distinction between these terms is widely recognized to be merely of semantic nature, as the notion that CB is subject to JT distortion persists tenaciously in the literature.[2,6,49] It should be pointed out, however, that there is a physical reason for this differentiation. If CB had indeed a truly degenerate ground state in D_{4h}, interconversion of two rectangular forms could never proceed via this highly symmetrical conformation. Basic group-theoretical arguments require that a lower-energy pathway leading through rhomboid structures always be available in this case,[l] excluding the square as a transition state.

It is interesting to note in this context that Halevi's OCAMS theory actually predicts a rhomboid transition state for the bond-switching process in CB.[46] While OCAMS is a very valuable tool in predicting the course of pericyclic reactions, it is operative within a one-electron approximation and therefore appears to fail in cases where this description becomes inappropriate as in the present CB case. The most extensive *ab initio* CI calculations performed to date (see Section 3.2) indicate that square CB in its ground state is indeed stable with respect to rhomboid distortions.

3.1.2 "*Anti-aromaticity*". The second term often used with little circumspection is "(anti-)aromaticity". This word is used to ascribe a set of chemical and physical properties, such as reactivity or thermochemical stability, to a certain group of molecules. Thus annulenenes can be divided into two subgroups that behave quite differently, namely those with (4n + 2) and those with (4n)π-electrons. For example, an external magnetic field induces opposite ring currents.[40] This effect, if used as a criterion to distinguish between the two subgroups (diamagnetic for aromatic and paramagnetic for anti-aromatic annulenes), offers certain advantages. First it rests upon a directly measurable quantity (^{1}H NMR), and second, it has a heuristically useful chemical implication: the appearance of a paramagnetic ring current can be rationalized in terms of an unusually small HOMO-LUMO splitting.[42] According to PMO-theory this feature is closely associated with a high reactivity, which is indeed a quality commonly attributed to all antiaromatic annulenes.

Another popular criterion for (anti-)aromaticity is based on thermochemical reasoning. It relates to the observation that [4n + 2]annulenes (especially benzene) are endowed with special stability by virtue of their cyclically conjugated π-systems. As it is commonly understood that [4n]annulenes should show opposite behavior to [4n + 2]annulenes, the former are often asserted to be "destabilized through cyclic conjugation". This notion is correct within the concept of "Dewar resonance energies",[95,96] according to which the π-bonding energy of a planar, antiaromatic annulene is smaller than that obtained from bond or group increments for linear polyenes. However, the presence of such "negative resonance energies" does *not* necessarily imply that disruption of cyclic conjugation would lead to a stabilization in these systems. This point is well illustrated by 1,5-bisdehydro[12]annulene, an [4n]annulene that is flexible enough to assume a conformation where cyclic conjugation can be actually disrupted. Recent investigations have shown that this antiaromatic ring system prefers to remain at a nearly planar conformation even at the cost of an increase in angular strain and van der Waals repulsions,[97] and is thus apparently *stabilized* through cyclic conjugation.

Maybe this effect is smaller in CB, but there is no *a priori* reason to assume that it is absent, nor that cyclic conjugation of its π-system should result in an (absolute) destabilization in this compound.[98] In addition, such reasoning refers to the π-system alone and implicitly assumes that cyclic conjugation does not result in any significant changes within the σ-framework. While this assumption is justified to a certain extent in benzene or the like where strain is unlikely to play a major role, the situation is more complicated in CB. The σ-electronic system of CB is of an entirely different nature than that of a linear polyene, and thus experimentally observed deviations from polyenic additivity can not be related to π-electronic effects as straightforwardly as in benzene.

---

[j] The term "second-order JT-effect" later introduced by Longuet–Higgins[91] is more appropriate. For a lucid outline of the mathematical reasoning that leads to this term (see Ref. 92).

[k] Note that it is not proper to rationalize this effect within one-electron approximation (for example HMO). Although bonding does in fact increase (by $2\times\delta\beta$ if $\pm\delta\beta$ is the change in β on introducing bond alternation), this effect is counterbalanced to an appreciable extent by increasing electron repulsion.[47,94]

[l] Unlike in cases with (2n + 1)-fold symmetry axes where stabilization occurs only along *one* (degenerate) normal mode, *two* different (non-degenerate) modes effect JT distortion if four-fold symmetry is present. For a D_{4h} species these two modes correspond to a rectangular and a rhomboid distortion, respectively, both of which necessarily induce a finite lowering of the total energy.[93]

Hence the concept of (anti-)aromaticity, which has proven to be very useful in spite of the difficulties associated with the definitions, must be used with caution in cases where one cannot easily disentangle stabilizing and destabilizing factors (see also Section 3.2.4).

3.2 *Computational results*

We now turn to a discussion of the computational results. Note that this review examines only studies performed after 1967. The reader should refer to the book by Cava and Mitchell[3] for a comprehensive discussion of the developments in the theoretical field prior to this date.

Table 4 summarizes the predictions with regard to energies and geometries of SS, ST and RS–CB, categorized according to the type of quantum chemical methods used. Blocks I and II show results of *ab initio* and semiempirical SCF-calculations, blocks IV and V list those obtained by methods that explicitly take electron correlation into account. Block III contains results of the intermediate approaches discussed in the text. For the sake of clarity only C–C and C=C bond lengths are compiled. Some of the studies actually included full geometry optimization, which can be of considerable repercussion to the shape of the hypersurface. For example, the early study by Buenker and Peyerimhoff[7] yielded a non-square "equilibrium geometry" for the triplet state of CB in contrast to all later findings. This is probably due to the fact that geometries were not optimized within their calculational scheme. Investigations including full geometry optimization are indicated in Table 4 by bracketed asterisks. In all other studies, reasonable C–H bond lengths and angles were assumed.

3.2.1 *Chronology.* First it seems appropriate to look briefly into the chronology of the appearance of these results in the literature.

After Chapman's and Krantz' IR spectral results were published, a theoretical rationalization was obviously needed for their findings consistent with the conclusion that CB was square. This need was satisfied by all *ab initio* calculations on the SCF level, which unanimously predicted a square triplet ground state, stable with respect to rectangular distortion.[78] Also, the singlet state never fell below ST in energy, though the former experienced some stabilization upon rectangular distortion.[101] However, when semiempirical methods were used, RS was found to be more stable than ST, and this result led Dewar to propose that CB might persevere as a *metastable* triplet under the conditions of cryogenic matrix isolation.[79,80] After ESR measurements had invalidated this explanation[37] (*vide supra*), a need suddenly arose to account for a square *singlet* state. However, a square singlet *minimum* would have contradicted all calculations, and the geometry of a CB derivative had proved to be a (slightly distorted) rectangle.[37] Therefore, efforts centered around the possibility of an "effectively square" singlet, i.e. a very shallow potential surface for the interconversion of two rectangular forms. Qualitative arguments indeed spoke in favor of this interpretation.[47] Subsequently, three groups independently engaged in extensive *ab initio* CI calculations on CB.[99,100,103] Their results unanimously supported Buenker and Peyerimhoff's earlier findings[7] (Type C potential surface in Fig. 1(b)) and clearly ruled out the possibility of an "effectively square" structure.

Since the recent reinvestigation of the IR spectrum produced results that stand in full agreement with these theoretical findings, theory and experiment were eventually reconciled again in 1978.

3.2.2 Hartree–Fock *treatment of square cyclobutadiene.* Since elucidating the reasons for the breakdown of a widely used theoretical model is more insightful than simply enumerating the results of more sophisticated procedures that have proved to be more sucessful, we shall discuss below in some depth the peculiarities which emerge from Table 4.

The most conspicuous discrepancy is that between the results obtained on an SCF level (blocks I and II) and those from the more elaborate CI-calculations (blocks IV and V). The SCF methods consistently yield a *triplet* ground state at square geometries, a prediction which looks reasonable at first sight as it conforms with Hund's rule. However, the fact that this ordering is inversed if correlation is taken into account leads to the conclusion that square CB can not be adequately described on an SCF level.

In fact, treatment of D_{4h} CB is not quite straightforward within the Hartree–Fock (HF) model because one has to deal with the special situation of two degenerate orbitals (hereafter denoted as ϕ_2 and ϕ_3) containing two electrons altogether.[106] These two electrons can be arranged differently to give six configurations that remain pairwise degenerate at a single-determinant SCF level. Designating the spatial part of the orbital by its index (2 or 3) and the spin part by a bar for β and no bar for α, these configurations can be represented as in Scheme 18.

$$|2\bar{2}| \qquad |3\bar{3}| \qquad |2\bar{3}| \qquad |3\bar{2}| \qquad |23| \qquad |\bar{2}\bar{3}|$$

Scheme 18.

Table 4.

Table 4a. Energies (kcal/mole) of SS and ST relatives to RS–CB

Block	Method (basis set)	Entry No. for Geometry	E(SS)	E(ST)	Remarks	Reference
I	STO-3G (SCF) (*)	1)	-	-3.73	a),b)	101
	4-31G (SCF)	2)	-	-5.40	a)	80
	6-31G* (SCF)	1)	-	-5.84	a),b)	101
	7.3/3 double ζ (SCF)	13)	(0)	-4.77	a)	103
II	SPO-π-SCF	5)	16.4	2.0	c)	6
	MINDO/3 (*)	6)	19.0	5.9	c)	79
III	6-31G* two determ.	7)	12.0	5.1	d)	99
	7.3/3 double ζ + SP	13)	(0)	9.8	e)	103
IV	STO-3G with π-CI	8)	4.2	22.4	f),g)	100
	6-31G* with π+σ-CI	7)	12.0	23.0	f)	99
	7.3/3 double ζ with IEPA	13)	13.4	22.0	f),h)	103
V	PPP-CI	11)	4.8	15.3	i)	9
	MC-π-LCAO	12)	6.9 (21.2)	14.0 (23.0)	i),j)	105

Table 4b. Geometry of SS, ST and RS–CB (bond lengths in Å)

Block	Entry	Method (basis set)	RS	SS	ST	Remarks	Reference
I	1)	STO-3G (SCF)(*)	1.313/1.569	-	1.431	a)	101
	2)	4-31G (SCF)	1.323/1.580	-	1.434	a)	102
	3)	7.3/3 double ζ (SCF)	1.321/1.605	1.444	1.441	a)	103
	4)	GVB	1.340/1.560	-	-	k)	78
II	5)	SPO-π-SCF	1.338/1.512	1.425	1.397	c)	6
	6)	MINDO/3 (*)	1.342/1.533	-	1.433	c)	80
III	7)	4-31G two determ.	1.334/1.564	-	-	d)	104
IV	8)	STO-3G with π-CI	1.369/1.539	1.453	1.451	f)	100
	9)	7.3/3 double ζ + SP	-	1.455	1.453	f),e)	103
	10)	7.3/3 double ζ + PF with CEPA	1.340/1.570	-	-	f),l)	84
V	11)	PPP-CI	1.331/1.498	1.427	1.422	i)	9
	12)	MC-π-LCAO	1.340/1.520	-	1.432	i)	105
VI	13)	presupposed geometry	1.340/1.520	1.440	1.440		103

[a] *ab initio* Calculations on the basis of single-determinant wave functions for RS and two-determinantal wave functions for SS and ST (see also text).

[b] It must be noted that the authors of this study pointed out that the small singlet-triplet splitting they obtained within their model actually suggests that the singlet ought to be the ground state of D_{4h} CB.

[c] Single-determinant semiempirical calculations.

[d] Two-configuration treatment not only for SS and ST but also for RS. Implications, see text.

[e] CI with singly excited configuration in order to account for spin polarization (SP). RS not included, hence SS is set to zero.

[f] *ab initio* Calculations allowing for correlation.

[g] On inclusion of σ-space CI, E(SS)–E(RS) rises to 8.3 kcal/mole.[100]

[h] E(ST) was calculated using the values for E(SS), ΔE_{SCF}(SS–ST) and E_{corr}(ST) found in the text and in different tables, yielding $-153.4172 - 0.0076 - 0.416 = -153.4664$ atomic units.

[i] Semiempirical CI-calculations.

[j] The values in brackets refer to a different parametrization scheme (see Footnote a and b in the caption for Table 5). There is some ambiguity in the figures for the singlet-triplet splitting: while Table 8 in[105] shows 0.272 eV for one and 0.306 eV for the other parametrization, Table 10 in[105] lists 0.317 and 0.316 eV, respectively. We used the average values in the Table.

[k] General Valence Bond method.

[l] PF refers to polarization functions that were added to the 7.3/3 double ζ basis set for carbon atoms. CEPA is a scheme that allows for correlation within a pair-correlation approximation.

Except for $|23|$ and $|\overline{23}|$, which represent the $m_s = +1$ and $m_s = -1$ components of the triplet state, it is not appropriate in the present case to use a single determinant description. While the two closed-shell configurations $|2\overline{2}|$ and $|3\overline{3}|$ can in principle be used to describe a pair of degenerate states, the corresponding wave functions suffer from the drawback that they cannot be classified within the D_{4h}

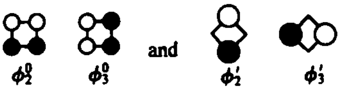
point-group.[7,106] Although this problem does not occur in $|2\bar{3}|$ and $|3\bar{2}|$, these determinants in turn do not represent proper anti-symmetrized wave functions and therefore violate the Pauli exclusion principle. In order to resolve these problems one has to determine which configurations will interact in first order. The result is that nonvanishing off-diagonal matrix elements occur only between the two sets of determinants $|2\bar{2}|/|3\bar{3}|$ and $|2\bar{3}|/|3\bar{2}|$. The negative combination of the latter two determinants then gives the $m_s = 0$ component of the triplet state.[m]

Thus, one obtains four states whose relative energies differ by the contributions due to the interaction of the two electrons in ϕ_2 and ϕ_3.[106] These contributions are listed next to the corresponding wave functions in the usual notation for Coulomb and exchange integrals ($J_{22} = J_{33} = J_{xx}$, $J_{23} = J_{32} = J_{xy}$ and $K_{23} = K_{32} = K_{xy}$):

$$
\begin{array}{l}
{}^1\psi_1 = N(|2\bar{2}| + |3\bar{3}|)\ldots J_{xx} + K_{xy} \\
\vdots \qquad\quad \vdots \qquad\quad . \qquad \vdots \\
\left.\begin{array}{l}
{}^3\psi_{+1} = |23| \\
{}^3\psi_0 = N(|2\bar{3}| - |3\bar{2}| \\
{}^3\psi_{-1} = |\bar{2}\bar{3}|
\end{array}\right\}\ldots J_{xy} - K_{xy}
\end{array}
$$

Scheme 19.

There is considerable confusion in the literature regarding the assignment of these states. While some authors define ${}^1\psi_3$ as the wave function of the lowest singlet state,[47m,94,100m,103] others claim that it is ${}^1\psi_2$.[104,108] The reason for this apparent contradiction is that in a two-determinantal treatment of square CB one is still free to choose between different real representations for ϕ_2 and ϕ_3. Two symmetry-adapted pairs are depicted in Scheme 20.



$\phi_{2,3}' = \frac{1}{\sqrt{2}}\cdot(\phi_2^0 \pm \phi_3^0)$

${}^{1,3}\psi_i^0 = f(\phi_{2,3}^0)$

${}^{1,3}\psi_i^1 = f(\phi_{2,3}^1)$

Scheme 20.

Authors who use the first set arrive at an energetic ordering of ${}^3\psi^0 > {}^1\psi_2^0 > {}^1\psi_3^0 > {}^1\psi_1^0$, while those using the primed set find ${}^3\psi' > {}^1\psi_3', {}^1\psi_2' > {}^1\psi_1'$. Evidently, ${}^3\psi_1$ and ${}^1\psi_1$ are invariant with respect to unitary transformations among the components of the degenerate orbital. As for the other two states, one can expand the corresponding determinants, substitute according to the formula in Scheme 20, and reassemble the nonvanishing terms in new determinants. Thus it can be proved that ${}^1\psi_2^0 \equiv {}^1\psi_3'$ and ${}^1\psi_3^0 \equiv {}^1\psi_2'$. Similarly expansion of the Js and Ks into integrals between atomic orbitals shows that $E({}^1\psi_2^0) = E({}^1\psi_3')$ and $E({}^1\psi_3^0) = E({}^1\psi_2')$. After evaluating the symmetry behavior of all four wave functions one arrives at a unique set of states (Scheme 21). Their relative energies obtained from calculations with a 6-31G* basis set[99] are included on the right end of Scheme 21 to show the magnitude of these figures.

symmetry[n]	wave function	relative energy[o]	calculated[99]
${}^1A_{1g}$	${}^1\psi_1^0 \equiv {}^1\psi_1'$	$J_{xx}^0 + K_{xy}^0 \equiv J_{xx}' + K_{xy}'$	67 kcal/mole
${}^1B_{2g}$	${}^1\psi_3^0 \equiv {}^1\psi_2'$	$J_{xy}^0 + K_{xy}^0 \equiv J_{xx}' - K_{xy}'$	60 kcal/mole
${}^1B_{1g}$	${}^1\psi_2^0 \equiv {}^1\psi_3'$	$J_{xx}^0 - K_{xy}^0 \equiv J_{xy}' + K_{xy}'$	7 kcal/mole
${}^3A_{2g}$	${}^3\psi^0 \equiv {}^3\psi'$	$J_{xy}^0 - K_{xy}^0 \equiv J_{xy}' - K_{xy}'$	0 kcal/mole

Scheme 21.

[m] Some authors[3,5a,47,100] use a *positive* combination of determinants to describe the $m_s = 0$ component of the triplet and a negative one for the open-shell singlet state. However, they use $|23|$ instead of $|32|$ which brings about an inversion of signs. It can easily be verified that the spin part of the triplet wavefunction is symmetric and the orbital part antisymmetric in both notations (and vice versa for the open-shell singlet).

[n] The assignment of ${}^1B_{1g}$ and ${}^1B_{2g}$ depends on how the twofold symmetry elements in D_{4h} are defined. We adopt the most widely used alternative where C_2' and σ_v bisect the bonds in the case of ϕ_2^0/ϕ_3^0 and the atoms in the case of ϕ_2'/ϕ_3' (and vice versa for C_2'' and σ_d).

[o] The relationships in column 3 can easily be proved within the ZDO approximation. Breakdown of the Js and Ks into contributions from atomic orbitals gives:

$$
\begin{array}{ll}
J_{xx}^0 = 0.25(\gamma_{11} + 2\gamma_{12} + \gamma_{13}) & J_{xx}' = 0.5(\gamma_{11} + \gamma_{13}) \\
J_{xy}^0 = J_{xx}^0 & J_{xy}' = \gamma_{12} \\
K_{xy}^0 = 0.25(\gamma_{11} - 2\gamma_{12} + \gamma_{13}) & K_{xy}' = 0
\end{array}
$$

A consequence of the identities $J_{xx}^0 = J_{xy}^0$ and $K_{xy}' = 0$ is that ${}^3\psi^0$ and ${}^1\psi_2^0$ (or ${}^3\psi'$ and ${}^1\psi_3'$) as well as ${}^1\psi_1^0$ and ${}^1\psi_3^0$ (or ${}^1\psi_1'$ and ${}^1\psi_2'$) are degenerate in ZDO. Depending on their choice of ϕ_2 and ϕ_3, various authors have attributed this fact to either of the two mentioned identities,[6,47,94,108] which lead, of course, to equivalent results.

A brief comment is inserted here with respect to semiempirical SCF-calculations on square CB. As outlined in Footnote *o*, $^3A_{2g}$ and $^1B_{1g}$ are degenerate in ZDO if a two-determinantal treatment is applied. The singlet-triplet splitting of 13.1 kcal/mole calculated with the (ZDO based) MINDO/3 procedure[79] resulted from the application of a ***single-determinant*** method, where the above degeneracy does not necessarily occur. However, the neglect of first order CI results in a state diagram that differs somewhat from that derived above (Scheme 21) and also emerging from all *ab initio* calculations. Within a single configuration scheme one obtains a degenerate pair of closed shell singlet states ($|2\bar{2}|/|3\bar{3}|$) not classifiable in D_{4h}, a B_{1g} triplet ($|23|$ or $|\overline{23}|$) and an open shell singlet (which was never explicitly considered). The practicability of a single determinant approach to this problem within RHF semiempirical methods has repeatedly been questioned.[79,47] All problems pertaining to the symmetry properties and relative energies of the configurations calculated in this way will be clarified in a forthcoming publication.[109]

Returning to the main course of discussion, readers may recall that application of *full* CI inverts the order of $^3A_{2g}$ and $^1B_{1g}$ obtained on a two-determinant level. A convincing rationale for this unique feature of square CB was first proposed by Borden[47,107] and was later outlined in more detail by Kollmar and Staemmler.[103] It is now clear that only in very special cases a *localized* real representation of degenerate orbitals (like ϕ_2' and ϕ_3') can be found in alternant hydrocarbons.[107] If two electrons populate such a set of orbitals, they can in fact be regarded as being confined to different regions of space. In the case of CB each of the electrons would then simultaneously occupy a different set of opposite carbon atoms in the four-membered ring.[p] If these two electrons now have antiparallel spins, they will induce a regional separation of the remaining electrons in other molecular orbitals of CB so that those with α-spin will gather in regions of space occupied by the α-electron in the NBMO and vice versa for the β-electrons, an effect called "spin polarization".[q] This effect is well-known in radicals and the resulting net spin densities can be traced experimentally by ESR. In CB this is of course not possible because *two* electrons induce spin polarization, and as their spin states are interchangeable any time, no net spin densities result. This consideration has led Kollmar and Staemmler to propose the term "dynamic spin polarization"[103] as opposed to the "static" variety encountered in radicals. If all α- and β-electrons are bound to occupy pairwise orbitals of the same shape as it is presupposed in the Restricted Hartree–Fock model (RHF), this spin polarization effect, mainly operative in the singlet, can obviously not be accounted for. Thus, the energy of SS is consistently overestimated in RHF SCF calculations.

How can this model-inherent error be corrected? The most straightforward way is to allow electrons of different spins to occupy different orbitals, an approach termed Unrestricted Hartree–Fock (UHF). Yamaguchi recently performed such a study[111] and found that indeed the order of stabilities is now reversed [E(SS)–E(ST) ≅ leV]. Unfortunately, a UHF treatment does not yield wave functions that can be properly classified according to integral spin quantum numbers (singlets, triplets...).[95] However, it is possible to conceive a procedure which mimics the energetic consequences of spin polarization without resorting to different orbitals for different spins. The procedure involves admixing RHF wave functions of singly excited configurations to that of ground state SS and ST. Kollmar and Staemmler demonstrated qualitatively that *one* singly excited configuration (obtained by promotion of an electron from ϕ_1 to ϕ_4) would take care of the overwhelming part of this spin correlation effect and indeed their calculations confirmed this.[103] Consequently, the singlet-triplet splitting was found to be 7.3–13.9 kcal/mole depending on the size of the basis set used. Their results are in full agreement with those of full CI-calculations listed in Table 4.

3.2.3 *The bond-switching process.* Let us now turn to rectangular CB. Here a normal single-determinant description is theoretically justified, because open-shell-configurations do not contribute to the ground state wave function in first order. Nonetheless, *ab initio* SCF-calculations still display somewhat peculiar features in that they predict a very high degree of bond alternation (R_{C-C} as in cyclobutane, $R_{C=C}$ as in ethylene), although very little energy is gained upon distortion from the square.

---

[p] The reader will notice that the entire discussion to follow rests on the particular choice of "localized" real representations for the pair of degenerate π-orbitals. A proper numerical treatment of square CB can of course be carried out using any linear combination of ϕ_2 and ϕ_3 and will always give identical results. However, the fact that fully localized real representations can be found permits an easily conceivable rationalization for the failure of the widely used RHF SCF-procedure in this particular case. In fact, Borden and Davidson have shown[107] that such a breakdown will always occur in cases where degenerate MOs can be confined to different centers.

[q] This effect is usually explained in terms of smaller repulsion between electrons of equal spin (accounted for via exchange integrals in HF-theory). While this explanation is very useful and leads to correct results, it is only valid within a "frozen orbital" approximation as used in RHF methods. On separate optimization of singlet and triplet wavefunctions, one finds[110] that repulsion is in fact *larger* for electrons of equal spin[110b] because their average distance is smaller than for electrons of opposite spin.[110a] It is the concomitant increase in nuclear-electron attraction that lowers the energy of triplets more than the corresponding singlets (unless special effects are operating as in the present case).

This result relates to the fact that the ground configuration ($|2\bar{2}|$ or $|3\bar{3}|$ using ϕ_2^0 or ϕ_3^0)[r] exhibits no π-bonding along the single bonds. Thus, the total π-energy increases steadily on distortion and deformation proceeds to a great extent. Eventually, a point is reached where the decrease in σ-bonding outweighs any further gain in π-bonding, but this point is only reached at a geometry with unreasonably long C–C bonds. As shown by Newton,[96] this situation can be rectified by admixing the lowest doubly excited configuration ($|3\bar{3}|$ if $|2\bar{2}|$ is the ground configuration, or vice versa) which will introduce some π-bonding along the single bonds, thus preventing an unduly strong deformation of the σ-frame. Again, full CI calculations, of course, also take this effect into account and therefore give reasonable bond lengths (for example, 1.37/1.54 Å in STO-3G with full π-space CI[100]).

In contrast to square CB, semiempirical RHF-methods can treat the rectangular species quite well, as shown, for example, by the reasonable geometry and energy (*vide infra*) predicted by MINDO/3.[79,80,102]

After having recognized that only CI procedures can account properly for the special effects operative in square *and* rectangular CB, their predictions with regard to the energy barrier for the bond switching process can now be discussed. Since two independent sets of calculations have demonstrated[99,100] that none of the excited states in square CB interact with $^1B_{1g}$ strongly enough to induce a rhomboid distortion, SS will be assumed to represent the transition state. All results then clearly rule out the possibility of an "effectively square" species[47,49,78] in accord with the new IR results.

The three most elaborate calculations presently available provide numerical values for the activation barrier that range from 8.3 to 13.4 kcal/mole.

In conclusion we wish to emphasize that recent efforts have resulted in a much clearer understanding of the unique electronic structure of this elusive species and have yielded an energy profile that is, at least qualitatively, in full agreement with experimental facts.

3.2.4 *The thermochemical stability of CB.* One aspect that has received relatively little attention from theoretical chemists concerns the overall thermochemical stability of CB, probably because virtually no experimental information is available in this respect. A knowledge of ΔH_f°(RS–CB) would be of considerable interest because this species undoubtedly comprises a unique combination of destabilizing effects which will be discussed separately in the following. Ironically, the least palpable of these effects has been most extensively covered in the literature. It is linked to the pragmatically useful but ill-defined notion of "antiaromaticity" (*vide supra*). Hückel[112] as well as SCF[113] π-procedures have predicted a wealth of different "negative resonance energies" for CB ranging from 0[8] to more than 30 kcal/mole.[114,s] In order to gain more reliable information, the problem was also attacked experimentally. But even if one relies solely on measurable quantities, any assessment of resonance energies is closely hinged on the type of reference structure chosen. Thus Breslow's experiments ingeniously designed to prove the presence of conjugative destabilization in CB[115] have recently been reinterpreted to indicate that CB might possibly have a small positive resonance energy.[98]

Turning to the second effect we note that CB is subject to considerable strain[116,117] which stems from 1,3 cross-ring interactions[118] and also to a lesser extent from angular deformation. A quantitative assessment of these contributions again depends on the reference structure.

A relatively unambiguous way to assess the energetic consequences of the *combined* destabilizing effects involves a comparison of ΔH_f°(CB) to a sum of terms obtained from an experimentally based increment scheme. Both Benson's group-increment[119] as well as Baird's bond increment scheme[96] arrive at a figure of ≃27 kcal/mole for this reference energy. The best estimate for ΔH_f°(CB) available at present comes from MINDO/3 (94.4 kcal/mole[79,80]). Since this method consistently underestimates the strain in 4-membered rings by 5–10 kcal/mole,[120] the true energy is expected to lie above 100 kcal/mole in accord with arguments which suggest that dissociation of CB into two acetylene molecules should be slightly exothermic[7] or roughly thermoneutral.[80] This implies that one will have to account for about 75 kcal/mole of destabilization, a high figure for such a small compound. Obviously, some experimental information on ΔH_f°(CB) is needed before one can try to offer an explanation for this theoretical outcome in terms of different effects.

3.2.5 *Excited states of CB.* Finally, we wish to turn to theoretical predictions dealing with excited states of CB. In order to be able to appreciate these, we would like to derive briefly what types of

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[r] In RS–CB there is no choice among different representations for the CB-orbitals. Within a single-determinant scheme ϕ_2^0 and ϕ_3^0 are the only appropriate canonical orbitals.

[s] Note that Hückel-methods are usually applied to *square* CB where such destabilization is presumably much more pronounced than in RS–CB. Most of the exceedingly high negative resonance energies therefore stem from HMO-procedures.

excited states are to be expected in the UV/VIS range for rectangular CB.[f] Using the orbitals ϕ_1 to ϕ_4 depicted on the right side of Fig. 5, we can construct a qualitative configuration diagram (note that a low-lying doubly excited configuration $^1A_g^*$ is to be expected due to the small energetic separation of ϕ_2 and ϕ_3)[*].

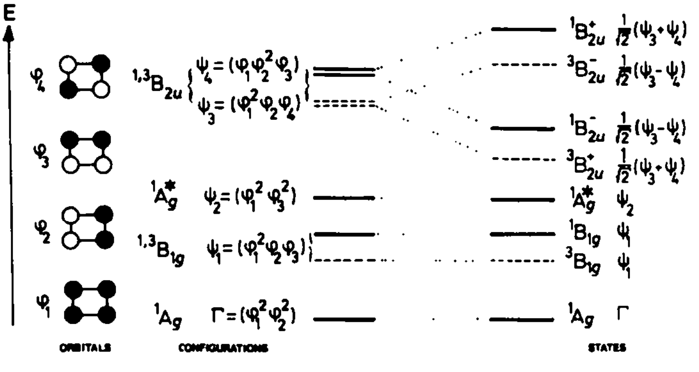

Fig. 5. Derivation of a qualitative state diagram for CB. Dashed lines refer to triplet, solid line to singlet states. (For the coordinate system, see Table 2).

At this level, the configurations arising through excitation $\phi_2 \rightarrow \phi_4$ and $\phi_1 \rightarrow \phi_3$ remain degenerate by virtue of the pairing properties inherent to alternant hydrocarbons which persist also at a single determinant SCF level.[122]

It turns out that electronic spectra cannot generally be explained at this level. But introduction of first order CI (accounting only for interaction between degenerate configurations) can usually correct this. It leads to a splitting of the four B_{2u} configurations. In the two singlets the interaction element is positive so that the minus combination will be lowered, while in the two triplets the corresponding matrix element is negative and the positive combination is the lowest.[123] Because the transition moments for excitation from ^1A_g are equal in the configuration diagram (another consequence of the pairing properties), they will cancel in $^1B_{2u}^-$, making the corresponding transition accidentally forbidden.[123]

Since the transitions to $^1B_{1g}$ and $^1A_g^*$ are dipole-forbidden at the equilibrium nuclear conformation and triplet states are usually not accessible through direct absorption, the qualitative diagram derived above already predicts that no strong bands should occur in the UV/VIS range. This result has been verified experimentally, and it has, in fact, helped to rule out ST–CB which ought to have a strong band in the visible[4,9] and should hence be colored.

However, vibronic coupling may well give rise to non-vanishing transition densities for excitation to $^1B_{1g}$ and the doubly excited state $^1A_g^*$. Although the latter will hardly be observable in normal absorption spectra, its position is of interest due to its possible role in the emission behavior of CB. Inspection of the orbitals in Fig. 5 shows that the HOMO–LUMO-splitting and hence the energies of $^{1,3}B_{1g}$ and $^1A_g^*$ relative to ^1A_g will depend strongly on the extent of rectangular distortion presupposed in a calculation. Furthermore, the π-SCF–CI procedures usually employed for the prediction of electronic spectra take geometrical variations mainly into account via the expression for the resonance integrals β. However, the choice of these expressions as well as their parametrization is by no means an unambiguous matter.

In view of these two points, it is not astonishing that the theoretical predictions summed up in Table 5 vary considerably with respect to the position of the $^1A_g \rightarrow {}^1B_{1g}$ and $^1A_g \rightarrow {}^1A_g^*$ transitions.

A closer inspection of the calculations by Downing and Michl[124] reveals that the description obtained by first order CI (Fig. 5) is actually fairly accurate for $^1B_{1g}$ and $^1B_{2u}^-$, i.e. they are virtually not contaminated by higher-lying configurations. Because the transitions $^1A_g \rightarrow {}^1B_{2u}^-$ can only gain "allowedness" (in D_{2h}) through higher B_{2u} configurations mixing into the target state, this implies that the corresponding band will be of very low intensity, as opposed to related biphenylene, where appreciable mixing with higher-lying configurations[125] results in a rather strong $^1A_g \rightarrow {}^1B_{2u}^-$ transition ($\epsilon = 10{,}000$).[126] On the other hand, weakly interacting ^1A_g and $^1A_g^*$ are both considerably lowered (0.58 and 0.77 eV, respectively) on applying full CI, thus demonstrating again the importance of doubly excited configurations for an accurate description of rectangular CB.

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[f] This derivation was recently generalized[121] to include all annulenes.

[*] Note also that $^1A_g^*$ does not lie twice as high above ^1A_g than the corresponding singly excited configuration $^1B_{1g}$ as one would expect on the basis of a simple Hückel model. Incidentally the pairing theorem gives equal electron densities in the HOMO and the LUMO, hence equal electron repulsion for ^1A_g and $^1A_g^*$ so that $E(^1B_{1g}) = 1/2\,E(^1A_g^*) - J_{23}$.

Table 5. Transition wavelengths (nm) and oscillator strengths for RS–CB

Method	$R_{C=C}/R_{C-C}$	$^1A_g \rightarrow {}^1B_{1g}$	$^1A_g \rightarrow {}^1A_g^*$	$^1A_g \rightarrow {}^1B_{2u}^-$	$^1A_g \rightarrow {}^1B_{2u}^+$	Ref.
MC-π I[a]	1.34/1.52	376 (0)	301 (0)	195 (0.14)	144 (0.67)	105
MC-π II[b]	1.35/1.52	465 (0)	428 (0)	218 (0.16)	140 (0.60)	105
PPP I[c]	1.33/1.52	487 (0)	439 (0)	192 (0.20)	-	4
PPP II[c]	1.33/1.50	507 (0)	471 (0)	198 (0.20)	125 (0.88)	9
EOM[d]	1.32/1.58	337 (0)	231 (0)	186 (0.00)	156 (0.04)	102
PPP[e]	1.34/1.57	352 (0)	285 (0)	172 (0.00)	148 (0.85)	104

[a] Semiempirical multiconfiguration π-LCAO method. Geometry optimized within this scheme; $\beta_{rs} = \beta_0 \cdot \exp[-a(R_{rs} - 1.397\ \text{Å})]$.

[b] Same as [a] but with a different expression for β. $\beta_{rs} = k \cdot S_{rs}$ (overlap between two p_z-orbitals on adjacent centers).

[c] PPP–CI, two different parametrizations. Geometries optimized within this scheme. The authors give no assignments for the transitions. They were made so as to give maximal accord with the other results.

[d] Equation of motion calculation on a 4-31G SCF wave function. The assignments for $^1B_{1g}$ and $^1A_g^*$ are in accord with those in the Table while the states reached in the transitions at 186 and 156 nm are termed B_{1u} in.[102] Geometry optimized on the SCF level with the 4-31G basis.

[e] PPP with full π-space CI: Geometry taken from the CEPA-study.[84]

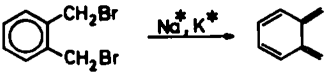
As far as a critical judgement of the results in Table 5 is concerned, we note that the observation of faint absorptions peaking at 425 nm [C_4(t-butyl)$_4$, C_4(t-butyl)$_3$COOCH$_3$] and 370 nm [$C_4(CF_3)_4$] suggests that the first transition in parent CB would not occur much above 350 nm. Thus only the calculations listed in the last two rows of Table 5 would be reconcilable with experiment.

4. OUTLOOK

As we have shown in the preceding sections, a great deal has been achieved in characterizing this elusive species during the past few years. Can cyclobutadiene therefore be considered as a "solved problem?" Obviously not. The most challenging problems are still awaiting further investigation, and in this section we wish to point out some of them and express a few thoughts on how they might be solved.

First we note that although evidence *against* a D_{2h}-species is absent, no positive experimental proof of the ground state geometry of CB has yet been given. The most obvious approach to this problem consists in an extension of our vibrational studies to include Raman spectra. Furthermore, much valuable information would emerge from a careful study of partially deuterated CBs. As mentioned, Chapman has measured the IR-spectra of d_1-, 1,2-d_2- and 1,3-d_2–CB,[77] but his findings do not agree exactly with those of Krantz in the case of d_1–CB[78] and obviously require reinterpretation in terms of non-square geometry in all three cases.

Theory predicts that CBs whose symmetry is lowered to C_s or C_2 by deuteration should exhibit a number of bands of fairly low intensity (as compared to those of CB and d_4–CB).[127] It therefore becomes paramount that no side products obscuring parts of the IR region are cogenerated. In view of this requirement, it might be rewarding to try to generate CB in a manner similar to that used by Michl *et al.* for the preparation of *o*-xylylene[128] as shown below.



Scheme 22.

This technique would possibly provide "cleaner" CB, which will certainly facilitate not only the detection of weak IR-bands but also the accurate recording of UV-absorptions of CB in the region critical for the evaluation of its electronic structure.

As we currently witness a strong surge of interest in polyene photophysics,[129] CB may be relevant in this context inasmuch as it also has a fairly low-lying doubly excited state. It would therefore be of considerable interest to look at the fluorescence spectrum and the excited state lifetime of CB and see whether the $^1A_g^*$-state has any odd effects on these properties, as observed recently in open chain polyenes.[129]

Equally or probably more important, experimental information concerning thermochemical parameters of CB are currently unavailable. These include the heat of formation of CB in its ground state and the barrier to interconversion of the two (probably) rectangular forms.

Considering the latter quantity it has been noted above that the activation energy for the bond-switching process is evidently very low in highly substituted derivatives.[43] The absence of steric repulsions in the parent compound suggests that the corresponding figure will lie in a region accessible to NMR measurements as predicted by theory.[99,100,103] However, it can easily be recognized that various difficulties have to be overcome in such experiments due to the high reactivity of CB. The advent of high-resolution solid-state NMR-techniques[130] is particularly encouraging and such methods will presumably find use for the solution of this problem. It requires a slightly perturbed CB such as its 1,2-dimethyl derivative obtainable in a matrix, where its two isomeric forms could be frozen out at cryogenic temperatures.

Finally, it is obvious that a knowledge of ΔH_f^0(CB) would be of great interest, for it would enable us to put the notion of antiaromaticity onto a more firm basis, if good estimates of strain contributions can be found (*vide supra*). Since thermochemical studies are not usually performed at cryogenic temperatures, there is little hope that CB will ever be subjected to such measurements. However, modern techniques of gas phase ion physics might show a way to the solution of this problem. If conditions for the generation of ground-state CB in the gas phase at low partial pressures can be found (for example, flash photolysis in the presence of a large excess of noble gas to allow quick thermalization without concomitant dimerization), it should be possible to measure the appearance potentials of the parent and maybe several fragment ions. This approach was recently used to determine the heat of formation of another reactive hydrocarbon, 3 radialene.[131] It can be used straightforwardly, provided that the ionic fragments are formed without (or with a known amount of) excess energy.

Note, however, that a mere knowledge of the adiabatic ionization energy of CB might suffice to arrive at the desired figure. A very careful recent study has shown that $\Delta H_f^0(C_4H_4^{\cdot+})$ obtained by photoionization of pyridine lies around 280 kcal/mole.[132] Since ΔH_f^0 of the most stable open chain $C_4H_4^{\cdot+}$-isomers (vinylacetylene and butatriene cation) are some 10 kcal higher, it has been concluded[132,133] that $C_4H_4^{\cdot+}$ observed in the dissociation of pyridine$^{\cdot+}$ (or benzene$^{\cdot+}$[133]) might well have a cyclic structure, hence correspond to CB$^{\cdot+}$. The structural identity of this fragment ion could be assessed through a determination of the collisional activation spectra of $C_4H_4^{\cdot+}$ obtained from CB and pyridine or benzene.

A measurement of $I_{a,1}$(CB) has already been attempted. Hedaya *et al.*[24] presented evidence supportive of the presence of free CB prior to ionization by electron impact. Appearance potential measurements led them to estimate of 8.2 eV for I_{a1}(CB).[v] Together with the mentioned 280 kcal/mole, this would lead to ΔH_f^0(CB) = 90 kcal/mole in reasonable agreement with theoretical predictions. The relatively broad energy distribution of the electrons used for ionization in conventional mass spectrometry results in a considerable uncertainty with regard to the exact threshold energy for ion formation.[136] Hence a reevaluation of this figure using monochromatic photons obtainable from synchroton radiation[137] is desirable to substantiate the above reasoning.

Another way of arriving at $I_{a,1}$(CB) would be by means of photoelectron (PE) spectroscopy. Recent developments in the application of this technique to the study of highly reactive species[138] appears to be encouraging and CB could possibly be subjected to such measurements as well.[w]

In addition to an independent measurement of $I_{a,1}$, the PE spectrum of CB will be intriguing in several other aspects. Firstly, CB$^{\cdot+}$ is now a truly Jahn–Teller active species, having a degenerate ground state in D_{4h}. However, this feature is not expected to manifest itself in the usual fashion (band shape),[139] because the transition occurs from an already "pseudo-Jahn–Teller" distorted neutral ground state, a rather peculiar situation. Secondly, the relatively small gap between ^1A_g and $^1A_g^*$ alerts us to look for a low lying non-Koopmans state in CB$^{\cdot+}$ which might interfere with a straightforward interpretation of the PE-spectrum of CB.

It is clear that both the existing problems outlined above and those which will emerge in the future are extremely challenging. The chemistry of cyclobutadiene has entered a stage where much higher levels of sophistication in both theory and experiment are demanded and the invention of newer

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[v] This figure is in good agreement with theoretical estimates[134] as well as with $I_{a,1}$ extrapolated from the PE spectra of CB–Fe(CO)$_3$.[135]

[w] Recently, endeavours in this direction have been undertaken by Schweig *et al.*[140] but so far they were not successful with respect to the observation of CB$^{\cdot+}$.

techniques appears to be indispensable for satisfactory solutions. These are challenges that scientists are willing to accept as they have done in the past. There is no doubt that continuing efforts will not only clarify the mystery of cyclobutadiene but at the same time will bring about a clearer understanding of many fundamentally important molecules as well.

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