Halogeno-substituted Cyclobutadienes. Molecular Orbital and Vibrational Frequency Calculations

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Molecular orbital and vibrational frequency calculations are reported for cyclobutadiene and various halogeno-substituted cyclobutadienes. It is suggested that the latter, especially the previously unreported perfluoro and perbromo compounds, should be thermally more stable than the parent compound and thus should be synthesized.

With the possible exception of benzene there has never been a molecule which has fascinated organic chemists, both theoreticians and experimentalists, as much as cyclobutadiene. Undoubtedly some of this interest is due to the difficulty of its synthesis, *e.g.* the first reported successful synthesis[1] came a century after initial[2] attempts; however, a greater part of the interest in this molecule can probably be attributed to its importance to our understanding of the concepts of resonance and molecular orbital theory.

Apparently the latter consideration can be summarized by the question, 'Is cyclobutadiene square?' If so, this would indicate that all four C–C bonds are equivalent, *i.e.*, intermediate between single and double bonds, and that the molecule is stabilized by resonance. If, on the other hand, the molecule is rectangular, this would indicate alternate single and double bonds, and therefore, at most, minimal resonance stabilization. In fact, molecular orbital calculations for many years have indicated that the lowest singlet state is rectangular and that the lowest triplet is square. On the other hand, experimental results on vibrational frequencies of C_4H_4, C_4H_3D[3a] and $C_4H_2D_2$[3b] were interpreted as indicating a square structure. The basis for this conclusion was that the number of peaks found[3a] was consistent with D_{4h} symmetry and not D_{2h}. In addition the spectra were interpreted[3b] as indicating the presence of only one isomer with deuteriums on adjacent carbons in the case of the $^2H_2$ compound, whereas a rectangular structure should have two such isomers (see Figure). These conclusions were further justified[4] theoretically by GVB results which indicated the triplet state to be more stable than the lowest singlet state by 7.7 kcal mol^{-1}. However, later i.r. determinations[5] on C_4D_4 showed absorptions not found[3a] previously which were inconsistent with a D_{4h} structure; a D_{2h} structure was indicated as most probable.

More recently[6] quite accurate theoretical calculations of the vibrational frequencies and intensities of the three possible rectangular [$^2H_2$]cyclobutadienes were performed and the results compared with Chapman's[3] experimental results. This group gave a different interpretation of the experimental results, *i.e.*, that Chapman had in fact observed a 1:1 mixture of the 1,2-$^2H_2$ and 1,4-$^2H_2$ isomers of cyclobutadiene.

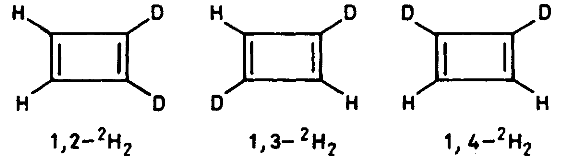
An extremely pertinent observation[7] which casts some doubt on the validity of the interpretation of the experimental vibrational frequencies is that all the experimental determinations use cyclobutadiene trapped on solid inert gas matrices at low temperatures and which has been produced from the photodissociation of 5-hydroxypenta-2,4-dienoic acid lactone (see Scheme). However, this reaction produces CO_2 in addition to cyclobutadiene, both substances being trapped in the matrix. Therefore one has to consider the possibility that absorption in the i.r. region can be due not only to C_4H_4, but also to either CO_2 or to a CO_2–C_4H_4 complex.

The major difficulty in interpreting the experimental vibrational spectra is the instability of cyclobutadiene, which leads to the rapid formation of various other products in the matrix which traps cyclobutadiene. These products range from the expected dissociation product, acetylene, to various adducts, such as Dewar benzene[8] and tricyclo-octadiene.[9]

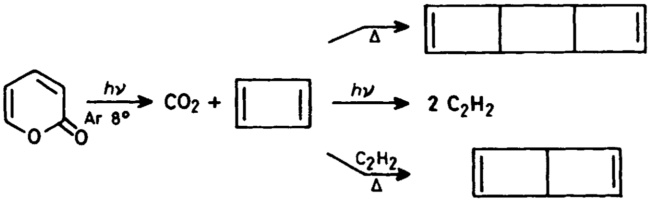
Thus the desirability of synthesizing more stable cyclobutadiene derivatives has been obvious for some time. In the past this has been done mainly by alkylating the carbons, with the idea of impeding dimerization because of the steric hindrance introduced. Although this tactic does diminish dimerization it suffers from the disadvantage of adding various atoms to the molecule, thus greatly increasing the complexity of the vibrational spectrum and the difficulty of its interpretation, in addition to having an effect on the 'strictly internal' modes. The objective of this study is to investigate the feasibility of the synthesis of cyclobutadiene derivatives (specifically halogenated cyclobutadienes) having the same number of atoms as the parent compound. In addition to the perhalogenated compounds we treat the interesting case of dihalogeno substitution, predicting relative stabilities and vibrational frequencies of the various possible isomers.

Methods

Relative stabilities of the various structures are calculated by the CNDO/2-FORCE[10] method which is ideally suited to the task of comparing structures which are quite similar, as treated here. The energy of each structure is taken[11] as that given by a



The three possible rectangular isomers of [$^2H_2$]cyclobutadiene



Scheme. Preparation and disappearance of cyclobutadiene linear extrapolation to the point where the sum of the absolute values of the various forces (3*N* for *N* atoms) converges to zero. This extrapolation is done by finding the *y*-intercept of the curve of energy *versus* $\sum_{i}^{3N}|F_i|$, using only those points where the sum of the absolute forces is equal to or less than 5 mdyne, *i.e.*, reasonably close to the calculated energy minimum. (Note that this method allows one to calculate the 'equilibrium' energy without having to arrive at the corresponding co-ordinates.)

The vibrational frequencies are calculated by a program written by one of the authors (O. M. H.) based on the Modified Valence Force Field method. The force constants were obtained by initially fitting the calculated vibrational frequencies for C_4H_4 ($^2H_0$ and $^2H_4$) to the four assigned experimental frequencies for each species. The $^2H_2$ frequencies were then calculated using the same force constants. The additional force constants necessary with the introduction of F and Br into the molecules were taken from the literature.[12]

The CNDO/2-FORCE calculations were done on a Burroughs B-6700 computer located at the Núcleo de Computção Electrônica, UFRJ. The vibrational calculations were divided between PDP-11 (UNICAMP), IBM 360/158 located at the Laboratório de Computações Científicas (CNPq), and B-6700 computers. All calculations used double-precision arithmetic.

Results and Discussion

(A) *Relative Stabilities*.—As a starting point we compared our CNDO/2 results to previously published[13–15] calculated and experimental results on the ground state of the parent hydrocarbon (see Table 1). Assuming that the experimental annular C–C distances for the totally substituted methyl tri-t-butylcyclobutadienylcarboxylate are the same as in the unsubstituted parent compound one observes that the CNDO/2 results are no worse than the *ab initio* results. However none of the three methods of calculation compared here does a particularly good job in predicting bond distances. (Note that the crowding of the t-butyl groups probably elongates the annular distances with respect to unsubstituted cyclobutadiene.) The most refined method (*ab initio*, using a 4-31G basis set) probably gives the worst results! Regarding the calculated relative stabilities of the square and rectangular structures, the STO-3G basis set gives the rectangular structure as being between 4.2 and 8.3 kcal mol^{-1} more stable, depending on the amount of configuration interaction introduced into the calculation. We calculate the rectangular structure to be 18.7 kcal mol^{-1} more stable, using only the HOMO–LUMO singly excited π orbital configuration in a configuration interaction calculation for the square structure. (The other π configurations make no appreciable contribution, nor does CI stabilize the rectangular structure in our calculations.) We know of no experimental determination of this value.

Table 1. Geometry of cyclobutadiene

Method	r/Å			HCC (°)	E_{square} − E_{rect}/kcal mol^{-1}	Ref.
	C=C	C–C	C–H			
STO-3G-CI	1.369	1.539	(1.1)[a]	(135)[a]	4.2—8.3[b]	13
4-31G-CI	1.334	1.564	(1.075)[a]	(135)		14
X-Ray[c]	1.376	1.506				15
CNDO/2	1.330	1.497	1.109		18.7	*d*

[a] Assumed values. [b] Value depends on amount of configuration interaction used. [c] Experimental work on methyl tri-t-butylcyclobutadienylcarboxylate. Distance given is shorter bond which is assumed to be less affected by steric hindrance. [d] This work.

Secondly we considered the known reactivity of cyclobutadiene (see Scheme) and calculated the energies for the various reasonable product structures, *i.e.*, acetylene, Dewar benzene, and tricyclo[4.2.0.0^{2,5}]octa-3,7-diene (*cis* and *trans*), plus the corresponding perfluoro and perbromo derivatives and some other mono-, di-, tri-, and tetra-fluoro- and -bromo-substituted derivatives of the above-mentioned compounds. In the case of the unsubstituted compounds we calculated the dimerization of cyclobutadiene to be exothermic by 16.5 eV, whereas the dissociation to give two acetylenes was found to be endothermic by 11.6 eV. These values are entirely consistent with the known experimental behaviour of cyclobutadiene (Scheme). Interestingly, we calculate the *cis*-form of the product of dimerization (tricyclo[4.2.0.0^{2,5}]octa-3,7-diene) to be more stable than the *trans*-form by 18.4 kcal mol^{-1}, consistent with the experimental[1b] findings that only the *cis*-isomer appears in the irradiation of 5-hydroxypenta-2,4-dienoic acid lactone. In addition, we find the hetero Diels–Alder addition of acetylene (almost certainly produced in the continued irradiation of cyclobutadiene) to cyclobutadiene to produce Dewar benzene to be exothermic by 3.4 eV, again in accord with the fact that Dewar benzene has been reported[8] to be found in the reaction mixture under conditions in which cyclobutadiene is produced but not isolated.

Having confirmed that in the case of the unsubstituted parent compound there is broad agreement between the calculated energies of the reagents and products, on the one hand, and the experimental kinetic results on the other, we are now ready to suggest that one can use this method of calculation to compare the relative propensities of two similar compounds to undergo the same reaction. This suggestion is based upon two assumptions: (1) for any two reactions being compared the kinetics will behave in the same way as the thermodynamics (independent of whether or not equilibrium is attained), *i.e.*, the more exothermic (less endothermic) product will also have a larger rate constant of formation, and (2) the CNDO/2 method is capable of correctly ordering the energies. Both of these assumptions are usually (although not always) true, and both will have an even greater tendency to hold in the case of the comparison of very similar molecules undergoing identical reactions, *i.e.*, the case being treated here.

In Table 2 one sees that for both of the two major pathways of destruction of the various halogeno-substituted cyclobutadienes that only perfluoro- and 1,3-difluoro-cyclobutadiene are more stable than the parent compound. In fact, these two compounds are calculated to be only slightly more stable with respect to dissociation, which is photochemical, and we suggest that it is unlikely that this extra stability would be noted. However, both these compounds are calculated to be appreciably more stable than the parent with respect to dimerization, the thermal process, and this difference should be experimentally verifiable.

Table 2. CNDO/2 Relative stabilities of halogenated cyclobutadienes

Compound		E/kcal mol^{-1}	
		Dimerization	Dissociation
C_4H_4		(0)	(0)
C_4F_4		88.2	1.9
C_4Br_4		161.3	−40.1
$C_4H_2F_2$	1,2; 1,4	37.0	−2.7
	1,3	55.0	3.9
$C_4H_2Br_2$	1,2; 1,4	21.6	−19.6
	1,3	70.0	−16.9

Table 3. Cyclobutadiene: $^2H_0$, $^2H_2$, and $^2H_4$ vibrational frequencies (cm^{-1})

$^2H_0$ Calculated				$^2H_4$ Calculated			1,2-$^2H_2$ Calculated			1,4-$^2H_2$ Calculated		1,3-$^2H_2$ Calculated		
a	*b*	Exp.	Repres. (D_{2h})	*a*	*b*	Exp.	*a*	*b*	Repres. (C_{2v})	*a*	*b*	*a*	*b*	Repres. (C_{2h})
737	585	586	b_{3u}	541	429	426	818	609	a_1	633	551	857	574	a_g
739	700	720	b_{2u}	632	527	608	1 056	846		906	771	954	702	
1 400	1 309	1 242		1 154	1 219	1 045	1 205	1 061		1 093	1 055	1 086	1 004	
3 425	3 053			2 519	2 264		1 712	1 483		1 332	1 271	1 272	1 077	
1 217	868		b_{1u}	876	626		1 783	1 577		1 729	1 566	1 730	1 566	
1 794	1 522	1 527		1 735	1 461	1 457	2 584	2 315		2 568	2 298	2 562	2 293	
3 425	3 063			2 554	2 300		3 444	3 069		3 444	3 064	3 436	3 063	
978	618		b_{3g}	924	564		575	483	b_1	609	486	669	691	b_g
1 322	1 083			1 067	907		764	777		979	839	980	879	
3 408	3 051			2 508	2 255		557	230	a_2	541	229	520	228	a_u
783	839		b_{2g}	617	666		887	760		708	711	669	490	
1 054	908		b_{1g}	843	728		1 064	980		1 010	965	1 009	940	
1 00[illegible]	827		a_g	778	593		681	554	b_2	928	580	672	562	b_u
1 2[illegible]1	1 085			1 074	1 035		956	640		981	725	995	794	
1 76[illegible]	1 597			1 697	1 539		1 106	995		1 284	1 029	1 349	1 268	
3 461	3 074			2 614	2 330		1 366	1 274		1 764	1 491	1 764	1 492	
616	243		a_u	507	216		2 514	2 259		2 532	2 278	2 538	2 282	
1 071	1 027			922	818		3 416	3 052		3 417	3 057	3 425	3 058	

[a] Ref. 6. [b] This work.

Table 4. Calculated vibrational frequencies (cm^{-1}) of the difluoro- and tetrafluoro-cyclobutadienes

		1,3-$C_4F_2H_2$			1,2-$C_4F_2H_2$			1,4-$C_4F_2H_2$	
C_4F_4	Repres. (D_{2h})	$^2H_0$	$^2H_2$	Repres. (C_{2h})	$^2H_0$	$^2H_2$	Repres. (C_{2v})	$^2H_0$	$^2H_2$
243	b_{3u}	382	359	a_g	217	216	a_1	216	215
191	b_{2u}	470	449		697	593		677	594
876		833	718		878	730		846	695
1 534		1 036	925		1 206	1 190		1 084	1 038
230	b_{1u}	1 302	1 300		1 561	1 507		1 330	1 324
917		1 746	1 715		1 803	1 800		1 750	1 725
1 759		3 063	2 299		3 068	2 314		3 063	2 297
354	b_{3g}	554	553	b_g	359	330	b_1	370	336
649		880	702		759	619		799	661
1 395		124	121	a_u	183	165	a_2	178	162
530	b_{2g}	468	402		657	643		629	606
577	b_{1g}	902	768		974	792		957	786
192	a_g	238	235	b_u	328	310	b_2	373	351
576		704	552		562	509		551	517
1 283		988	913		825	744		889	742
1 838		1 316	1 274		1 181	1 084		1 212	1 164
90	a_u	1 704	1 685		1 488	1 481		1 765	1 735
746		3 058	2 285		3 052	2 260		3 058	2 284

(B) *Vibrational Frequencies.*—Table 3 shows our vibrational assignments for C_4H_4, C_4D_4, and the three $C_4H_2D_2$ isomers, compared with other calculated[6] and experimental[5] results, where these latter have been assigned. (Note that although experimental frequencies have also been published[3b] for the three $C_4H_2D_2$ isomers, there is some question regarding the origin of the bands attributed to the 1,2- and 1,4-structures and the frequencies determined for the 1,3-structure have not been assigned, rendering them, in our view, of little value for comparison with calculated values.)

In comparing our calculated results to those of Schaad *et al.*[6] it is evident that not only are our frequencies better in the case of the eight experimental values where our data were fitted (*i.e.*, we attain an r.m.s. difference of 72 cm^{-1} whereas Schaad's[6] r.m.s. difference is 167 cm^{-1}), which is to be expected, but also those frequencies which have basically one component are closer to their usual values in our calculations. For example the four predominantly C–H stretches in C_4H_4 ($^2H_0$) we calculate to vary from 3 051 cm^{-1} to 3 074 cm^{-1}, whereas Schaad's values[6] are some 400 cm^{-1} higher. (The expected values are approximately 3 000—3 100 cm^{-1}.) In the same molecule the predominantly C=C stretch (a_g) for which we have no experimental value we calculate to vibrate at 1 597 cm^{-1} whereas Schaad calculates the vibration to have a frequency of 1 764 cm^{-1}. (The expected experimental value is 1 620—1 680 cm^{-1}.) The three predominantly HCC bends we calculate to have frequencies of 827, 868, and 1 083 cm^{-1}, whereas Schaad calculates the corresponding frequencies to be 1 008, 1 217, and 1 322 cm^{-1}. (The expected experimental frequencies are 700—1 000 cm^{-1}.) Thus one is almost forced to conclude that our vibrational calculations yield better frequencies than those previously published.[6]

In Table 4 we give the calculated vibrational frequencies for the perfluoro- and difluoro-cyclobutadienes, whereas Table 5 gives the corresponding data for the perbromo- and dibromo-

Table 5. Calculated vibrational frequencies (cm^{-1}) of the dibromo- and tetrabromo-cyclobutadienes

C_4Br_4	Repres. (D_{2h})	1,3-$C_4Br_2H_2$ $^2H_0$	1,3-$C_4Br_2H_2$ $^2H_2$	Repres. (C_{2h})	1,2-$C_4Br_2H_2$ $^2H_0$	1,2-$C_4Br_2H_2$ $^2H_2$	Repres. (C_{2v})	1,4-$C_4Br_2H_2$ $^2H_0$	1,4-$C_4Br_2H_2$ $^2H_2$
167	b_{3u}	196	196	a_g	98	97	a_1	96	96
82	b_{2u}	360	328		384	375		383	375
539		745	638		857	621		837	611
1 357		1 047	920		1 131	1 110		1 084	1 039
102	b_{1u}	1 159	1 156		1 550	1 496		1 183	1 182
527		1 654	1 621		1 677	1 672		1 656	1 626
1 630		3 063	2 296		3 069	2 316		3 063	2 296
177	b_{3g}	501	500	b_g	310	286	b_1	326	296
532		879	703		742	597		793	651
1 077		77	75	a_u	169	150	a_2	161	145
473	b_{2g}	458	393		627	615		595	573
532	b_{1g}	892	756		976	792		948	776
78	a_g	146	143	b_u	241	227	b_2	280	264
229		478	440		435	409		416	397
1 176		836	659		706	622		766	659
1 706		1 307	1 257		1 075	974		1 038	938
37	a_u	1 590	1 567		1 336	1 306		1 689	1 651
725		3 058	2 283		3 052	2 259		3 058	2 284

Table 6. Force constants used (mdyn Å^{-1})

Stretches	CH	CF	CBr	CC	C=C
	5.07	6.49	3.12	3.60	8.50
Bends	FCC	HCC	BrCC	CCC	
	0.79	0.54	0.94	0.84	
Wags	FC	HC	BrC		
	0.47	0.23	0.55		
Torsion	C–C	C=C			
	0.15	0.20			
Off-diagonal	C–C···C–C		C=C···C=C		
	0.51		0.80		

compounds. Table 6 shows the final values of the force constants employed.

Conclusions.—The necessity of synthesizing more stable cyclobutadienes has been recognized for several years. We suggest that the halogeno-substituted cyclobutadienes, especially their perhalogeno and dihalogeno compounds, should be considerably more stable thermally, and thus would be ideal candidates for preparation. Based upon empirical experience one would venture the suggestion that the fluoro compounds would be better candidates than the bromo compounds because the former should be less subject to halogen–carbon bond rupture.

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