

on the accuracy of the available experimental parameters.

Some comments on the $\gamma \sim \chi^{-2/3} \sim \beta^{2/3}$ relationship may be of value. For liquid metals, the surface tension was correlated¹¹ with the plasma frequency, ω_p , and thereby can be correlated with surface plasmons, ω_s ,¹⁴ so that

$$2\omega_s^2 = \omega_p^2 = 3Ze^2/mr^3 \quad (6)$$

where Z is an effective valence, m is the electronic mass, and r is the size of the atom. (Equation 6 may be used also to calculate the surface tension of binary alloys.¹²) It was suggested earlier⁴ that the surface tension was proportional to a surface elasticity, i.e., with $\beta^{2/3}$ dependence, the two-dimensional analogue to the three-dimensional bulk modulus. Consider the frequency of the optical branch of a one-dimensional lattice with two kinds of atoms given by¹³

$$\omega^2 = 2\mu(1/m + 1/M)$$

where μ is an elastic stiffness coefficient and m and M are the masses of the atoms. When one of these is taken as an electron this becomes

$$\omega^2 \approx 2\mu/m \quad (7)$$

For liquid metals when $\beta^{2/3}$ is used for μ , the frequency from eq

7 is in reasonably good agreement⁴ with those obtained from eq 6. This might be expected since the average of the three bulk stiffness coefficients is very nearly equal to the bulk modulus [see tables of values in ref 13]. Thus, the relationship between bulk modulus and surface tension, i.e., $\gamma \sim \beta^{2/3}$, may be considered to follow as

$$\omega_p^2 \sim \omega^2 \sim \mu \sim \beta^{2/3} \sim \gamma$$

It may, therefore, be anticipated that other liquid surface tension followed in the same manner. For a first consideration of organic liquids, it is difficult to imagine a liquid metal type of plasma oscillation. However, according to the London dispersion effect, after interaction between two oscillators, each vibrates with different frequencies, one greater than and the other less than their original frequency, ω_0 , or

$$\omega^2 = \omega_0^2 \pm 2e^2/mr^3 \quad (8)$$

where m is the electronic mass and r is the separation between oscillators.¹⁴ For these oscillations the positive pole of the dipole moment (permanent or induced) of one oscillator will be coupled to the negative pole in an adjacent oscillator. This is analogous to the plasma frequency in a liquid metal. Indeed, when $Z = 1$ in eq 6, it becomes very nearly the dispersion effect of eq 8. This suggests that any fundamental development of surface tension must incorporate the London approach.

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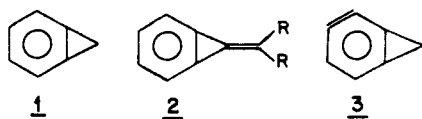
Cyclopropabenzene. Geometry, Electronic Structure, Strain, Reactivity, and the Question of Bond Fixation. A Theoretical Study[†]

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Abstract: Molecular orbital calculations, both semiempirical (MINDO/3 and MNDO) and ab initio (STO-3G, 3-21G, and 3-21G*), for cyclopropabenzene (**1**) and for several 7-mono- and -disubstituted derivatives are reported. The geometry, electronic structure, strain, reactivity, and the question of bond fixation in **1** are discussed in light of the computational results. The calculated ab initio geometries are in good agreement with experiment, and the 7-substituents have a very small effect on the structure of **1**. The semiempirical methods produce erroneous geometries. In particular the fused bond is too long. The calculated bond lengths in **1** at 3-21G* are (in Å) C₁-C₆ = 1.333, C₁-C₂ = 1.372, C₂-C₃ = 1.400, C₃-C₄ = 1.396, and C₁-C₇ = 1.495. The bond angles around the bridge bond are severely distorted: $\angle C_6C_1C_2 = 124.7^\circ$ and $\angle C_1C_2C_3 = 113.1^\circ$. The reactions of **1** are rationalized by FMO theory as being controlled by the HOMO which is localized at the bridge bond, which therefore is the preferred site for reaction with electrophiles and electron-poor dienes. Both the semiempirical and the ab initio calculations reproduce well the experimental strain energy in **1** of 68 kcal·mol⁻¹. It is concluded that the concept of bond fixation provides little help in understanding either the geometry (which is not consistent with either of the conventional benzene Kekulé structures or with the π -population) or the reactions of **1**.

Strained organic molecules have always fascinated chemists and experimentalists¹ as well as theoreticians.² Three-membered rings have attracted special attention because of the severe enforced angle deformation,^{1,2} and cyclopropabenzene (**1**) is of particular interest in this context. The fusion of the two rings in **1** is expected



to result in considerable distortion of the benzene ring. Furthermore, its aromatic stabilization may be reduced by bond fixation.^{3,4} Cyclopropabenzene and its derivatives can be now

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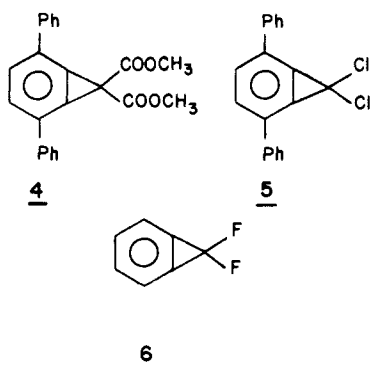
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[†]Dedicated to Prof. John A. Pople on the occasion of his 65th birthday.

prepared relatively readily and their application as synthons in natural product synthesis has raised considerable interest.⁴ Recently, new interesting derivatives of **1**, methylenecyclopropabenzene (**2**)^{5a} and both of the possible *o*-cyclopropabenzynes, e.g., **3**,^{5b} were synthesized by Halton's group.^{5a,b}

Despite the accessibility of **1** and the general interest in the structures of cyclopropane and cyclopropene derivatives,⁶ its geometry remains unknown. The structures of three cyclopropabenzene derivatives **4–6** have been determined experimentally (**4**⁷ and **5**⁸ by X-ray crystallography and **6**⁹ by microwave spectroscopy). The structure of the higher homologue, cyclo-



propanaphthalene, has been also determined.^{4c} However, it is not clear whether **4–6** are good models for deducing the geometry of **1** because these derivatives are heavily substituted.⁶ Despite the significant interest in cycloproparenes⁴ and their derivatives,⁵ and in particular in the possibility of bond fixation,^{3,4} it is surprising that at the time that this study was carried out, except for a single case, there were no other molecular orbital studies of this intriguing molecule. This case was concerned with a single-point STO-3G calculation of **1** which used an assumed geometry.¹⁰ An MNDO calculation of **6** was reported along with many other molecules, but an analysis or discussion of the results was not included.^{10b} When this paper was in the hands of the referees, Hiberty et al. (HOD) published in this journal an interesting valence-bond study of cyclopropabenzene,¹² and their results are discussed below.

We report here both semiempirical and ab initio calculations for cyclopropabenzene and for several of its derivatives. We discuss the geometry, the electronic structure, the strain energy, the reactivity, and the question of bond fixation in **1**. We also comment on the reliability of the various theoretical methods, a point which is of importance for future studies of higher homologues, where ab initio calculations are prohibitive. Calculations for **2**, **3**,^{5c} and other related systems will be reported separately.

Methods and Results

We have used both semiempirical (i.e., MINDO/3^{11a} and MNDO^{11b}) and ab initio methods. At the ab initio level we used the Gaussian series of programs^{13a} with three basis-sets: the

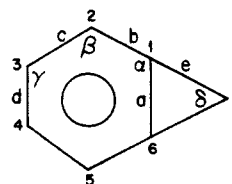


Figure 1. Geometrical parameters and atom numbering for cyclopropabenzene (**1**).

minimal STO-3G basis set,^{13b} the split-valence 3-21G basis set,^{13c} and the polarized 3-21G* basis set.^{13d} The 3-21G* basis set includes a set of six d functions (identical with the set used in the larger 6-31G* basis set^{13e}) on all non-hydrogen atoms.^{13f} The structure of cyclopropabenzene (**1**) was fully optimized at all levels of theory up to 3-21G* (at 3-21G*, the C–H bond lengths were held at the 3-21G distances) using gradient techniques.^{13a} Several 7-mono- and disubstituted cyclopropabenzene (**1a–1f**) were also calculated. These molecules were fully optimized with MNDO. At the ab initio level, only the monosubstituted derivatives were examined and the geometries were partially optimized.



- 1**, $R_1 = R_2 = H$
1a, $R_1 = H, R_2 = F$
1b, $R_1 = R_2 = F$
1c, $R_1 = R_2 = Cl$
1d, $R_1 = H, R_2 = -CHO$
1e, $R_1 = H, R_2 = CN$
1f, $R_1 = R_2 = CN$

The resulting geometries are reported in Table I, and the definitions of the geometrical notations are presented in Figure 1. The calculated heats of formation (MINDO/3 and MNDO) and the total ab initio energies are also reported in Table I.

Discussion

a. The Question of Bond Fixation. How does the fusion of the cyclopropene ring distort the benzene ring? A conceptually interesting possibility is that the fusion of a small ring to benzene might cause partial double-bond fixation in the aromatic ring. The hypothesis of such bond fixation in the direction indicated by **7a** was first advanced by Mills and Nixon in 1930 to explain certain differences in the chemical reactivities in indan (**7**, $n = 3$) and tetralin (**7**, $n = 4$).¹⁴ Although the experimental data on which this hypothesis was based were subsequently shown to be ambiguous,¹⁵ an early theoretical study of indan led Coulson and Longuet-Higgins to conclude that bond length alternation should indeed occur and be more pronounced as the size of the annulating ring decreases but in an "Anti-Mills–Nixon" sense, i.e., as indicated by **7b**.¹⁶ However, subsequent theoretical investigations reversed this conclusion, suggesting that in **1** structure **8a** is dominant,¹⁷ as originally proposed by Mills and Nixon.¹⁴

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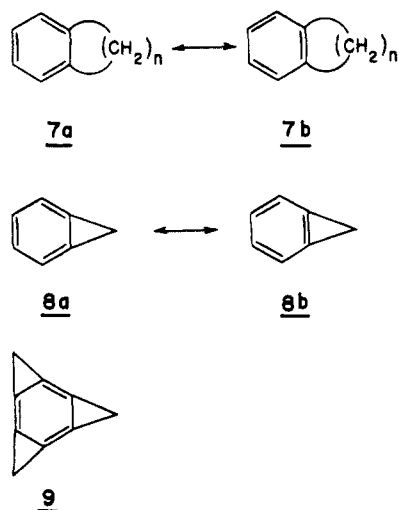
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The question of bond fixation has continued to attract both theoreticians and experimentalists also in recent years. Mitchell et al. have demonstrated in a beautiful NMR experiment the absence of significant π -bond localization in dihydropyrenes annelated with two four-membered rings.¹⁸ On the other hand, in a very recent valence-bond study, HOD computed the weights of the Kekulé (8a, 8b, and others) structures of **1** and found strong bond fixation favoring structure 8a.¹² Similarly an MNDO study of tris(cyclopropabenzene) indicated strong bond fixation as indicated in **9**.¹⁹

In this study, we do not intend to reinvestigate theoretically or to solve the long controversy raised by the question of bond fixation. We wish to examine whether the theoretically predicted bond localization¹² is reflected in the geometry or in the chemical behavior of cyclopropabenzene or whether some other analysis is more useful for understanding the properties of this intriguing molecule.² This question is of major interest whether the concept of bond fixation is theoretically valid¹² or not.¹⁸

It is important to note that cyclopropabenzene plays a central role in the bond fixation hypothesis because it is considered to be the best candidate for exhibiting this phenomenon in the series of monoannulated aromatics.^{4,12,16} The disagreement between HOD's theoretical conclusions¹² and Mitchell's NMR¹⁸ results was rationalized in this manner.¹² The absence of bond localization in **1** implies that this phenomenon is unimportant also in other (particularly less strained) annelated aromatics.

b. Geometry. Geometry was used in most previous studies as an important criterium for bond fixation.^{14,16-18} According to this criterium, a bond shortening is associated with increased importance of the structure bearing a double bond on that particular linkage. Knowledge of the precise geometry of cyclopropabenzene is therefore of prime importance. However, this geometry is not known experimentally, and the use of the available structures, which include only heavily substituted derivatives (**4-6**), as models for **1** is questionable. Thus, substitution, in particular that of carbomethoxy and fluorine, effects strongly the geometry of the cyclopropane ring,⁶ and it may also change the relative contributions of the Kekulé structures (8a and 8b in **1**, 7a and 7b in the general case). We anticipated that a reliable geometry of **1** can be obtained by molecular orbital calculations.

Examination of Table I reveals a dramatic difference between the semiempirical and the ab initio geometries. The bridge bond *a* (Figure 1) is much shorter according to the ab initio calculations than according to the semiempirical methods [*a* = 1.452 (MINDO/3), 1.427 (MNDO), 1.343 (STO-3G),²⁰ 1.337 (3-21G),

and 1.334 Å (3-21G*)]. CNDO/2 like the other semiempirical methods gives a long *a* bond of 1.420 Å.^{17b} The differences between the theoretical methods are less pronounced for the other geometrical parameters, excluding bond *c* which is significantly shorter according to the ab initio calculations (Table I). Concentrating on bond *a*, the semiempirical calculated geometries support bond fixation in the direction shown in 8a, while the ab initio calculations imply bond fixation in the opposite sense, i.e., as in 8b. Which of these geometries is correct? The experimental geometries of **4**,⁷ **5**,⁸ and **6**⁹ with bonds *a* in the range of 1.33–1.36 Å appear to support the ab initio calculations. However, reliable conclusions can be reached only if the effect of substitution on distance *a* is evaluated. We have therefore studied several substituted cyclopropabenzenes (**1a-1f**), where the substituents were selected so as to model the experimental systems. Thus, **1b** and **6** are identical, **1c** models **5**, and **1d** models **4**. The calculations for **1a-1f**, both the semiempirical and the ab initio (Table I), demonstrate that the effects of these substituents on distance *a* are relatively small, less than 0.015 Å. These substituent effects are considerably smaller than in the corresponding cyclopropane derivatives,⁶ probably as a result of the high rigidity of **1** where a change in *a* may increase the strain in the other bonds.

The small effect of the 7-substituents on *a* suggests that the measured distances for the fused bonds in **4-6** are close to that in the parent **1**. For **1** we calculate that *a* = 1.337 Å at 3-21G and 1.334 Å at 3-21G*. The addition of correlation energy usually elongates bond lengths by 0.01–0.03 Å, in particular multiple bonds.²¹ For cyclopropene we calculate C=C bond lengths of 1.282 and 1.276 Å at 3-21G and 6-31G*, respectively, compared with the experimental value of 1.296 Å.²² On the basis of this information and related previous experience, we estimate that in **1** the fused bond length is 1.35–1.36 Å. This estimate is in good agreement with the experimental values in **4-6**, especially if the substituent effects are taken into consideration.²³ Thus, in **4**, *a* = 1.333 Å, but the calculations for **1d** show that two carbonyl substituents at C₇ shorten bond *a* by 0.015 Å. Similarly, in **6**, *a* = 1.339 Å but the *gem*-difluoro substituents are expected to shorten this bond by 0.01 Å (see calculations for **1a** and **1b**). In **5**, *a* = 1.35 Å in agreement with the predicted negligible change in *a* by the chlorine substituents (see **1c**).

On the basis of the discussion above, we can state with confidence that the ab initio calculations that give a short *a* bond are correct, while the MNDO, MINDO/3 and CNDO/2 calculations that predict a much longer *a* bond are misleading. This conclusion calls for great caution in applying these semiempirical methods to the study of geometries of highly strained systems (e.g., the homologues of **1**). Furthermore, previous studies of annelated aromatics which used these methods should be reexamined. One example is **9**, where MNDO calculations predict strong bond fixation.¹⁹

Does the geometry of cyclopropabenzene reveal bond fixation? Bond *a* (1.337 Å at 3-21G) is much shorter than standard sp²–sp² C–C single bonds (e.g., 1.467 Å in butadiene at 3-21G) or than the C–C bond in benzene (1.384 Å at 3-21G). The relatively short *a* bond which is almost identical with that in ethylene (1.315 Å at 3-21G) may point to bond fixation in the direction indicated by 8b. However, although bond *a* is shorter than the C–C bond in benzene, it is 0.055 Å longer (at 3-21G) than the C=C distance in cyclopropene, indicating significant contribution of resonance structure 8a (the bond lengthening on going from ethylene to benzene is similar, i.e., 0.07 Å at 3-21G). Furthermore, bond fixation according to 8b requires that bonds *a* and *c* should be shorter than bonds *b* and *d*. This requirement holds for bond *a* but not for bonds *b*, *c*, and *d*. Bond *b* is shorter by ca. 0.04 Å than bond *c* (Table I), and *c* and *d* are similar to the C–C distance in benzene. Furthermore, the extensive study by Haddon and

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(20) Our STO-3G geometry is essentially identical with that reported by HOD.¹²

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(23) We assume that the effect of the ring phenyl substituents is small.

Table I. Calculated Geometries and Energies of Cyclopropabenzene (1) and of Several 7-Substituted Cyclopropabenzene Derivatives (1a–1f)^a

compd	7-substituents	method	geometrical parameters ^b								C ₇ -R	other parameters	energy ^c	
			a	b	c	d	e	α	β	γ				δ
1	R = R' = H	MINDO/3	1.452	1.377	1.429	1.400	1.474	122.4	115.3	122.3	59.0	1.111	f	80.2
1	R = R' = H	MNDO	1.427	1.361	1.441	1.398	1.499	124.1	113.2	122.7	56.8	1.098	g	89.7
1	R = R' = H	STO-3G	1.343	1.376	1.403	1.391	1.498	124.7	112.8	122.5	53.3	1.089	h	-265.18332
1	R = R' = H	3-21G	1.337	1.362	1.406	1.390	1.517	124.8	113.1	122.2	52.3	1.075	i	-266.95282
1	R = R' = H	3-21G*	1.333	1.372	1.400	1.396	1.495	124.7	113.1	122.4	52.9	j	j	-267.20478 ⁱ
1a	R = H, R' = F	MNDO	1.420	1.363	1.438	1.400	1.517	124.3	113.0	122.9	55.8	1.335	k	44.67
1a ^d	R = H, R' = F	3-21G	1.339	1.366	1.406 ^d	1.390 ^d	1.488	124.6	113.1 ^d	122.2 ^d	53.5	1.382	l	-365.27345
1b	R = R' = F	MNDO	1.419	1.364	1.438	1.402	1.524	124.4	112.7	122.9	55.5	1.338	m	-1.41
1c	R = R' = Cl	MNDO	1.423	1.365	1.437	1.402	1.493	124.4	112.7	123.1	56.9	1.772	n	78.91
1d ^e	R = H, R' = CHO	MNDO	1.423	1.360	1.441	1.398	1.504	124.4	112.8	122.8	56.5	1.513	o	60.52
1d ^{d,e}	R = H, R' = CHO	3-21G	1.331	1.362	1.406 ^d	1.390 ^d	1.519	125.0	113.1 ^d	122.2 ^d	52.0	1.489	p	-379.04077
1e	R = H, R' = CN	MNDO	1.420	1.362	1.441	1.399	1.508	124.5	112.7	122.8	56.2	1.443	q	123.08
1e ^d	R = H, R' = CN	3-21G	1.329	1.362	1.406 ^d	1.390 ^d	1.518	125.1	112.6	122.2 ^d	51.9	1.440	r	-358.16765
1f	R = R' = CN	MNDO	1.413	1.362	1.440	1.401	1.519	124.7	112.4	122.9	55.6	1.449	s	160.76

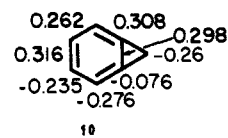
^aThe geometrical parameters are defined in Figure 1. The existence of a plane of symmetry passing through C₇ and the middle of bonds C₁-C₆ and C₃-C₄ was assumed. D.M. stands for the calculated dipole moment in debyes. ^bBond lengths in angstroms; bond angles in degrees. ^cIn hartrees for the ab initio calculations. For MNDO and MINDO/3, the calculated heats of formation (in kcal·mol⁻¹) are given. ^dOnly a, b, e, r(C₇-R), α, β, and γ were optimized. ^eThe most stable conformation around the C₇-CHO bond is given. ^f∠HC₇H = 111.3, ∠HC₂C₁ = 125.4, ∠HC₃C₂ = 118.0, r(C₇-H) = 1.099, r(C₂-H) = 1.087, r(C₃-H) = 1.091, D.M.^a = 0.06 D. ^g∠HC₇H = 111.3, ∠HC₂C₁ = 125.3, ∠HC₃C₂ = 118.0, r(C₇-H) = 1.098, r(C₂-H) = 1.086, r(C₃-H) = 1.091, D.M.^a = 0.06 D. ^h∠HC₇H = 112.6, ∠HC₂C₁ = 125.5, ∠HC₃C₂ = 119.2, r(C₂-H) = 1.083, r(C₃-H) = 1.083, D.M.^a = 0.07 D. ⁱ∠HC₇H = 115.2, ∠HC₂C₁ = 125.2, ∠HC₃C₂ = 119.1, r(C₂-H) = 1.070, r(C₃-H) = 1.072, D.M.^a = 0.07 D. ^jAll C-H bond lengths were kept at the 3-21G values. ^k∠HC₇H = 113.5, ∠HC₂C₁ = 125.3, ∠HC₃C₂ = 119.2. ^l∠HC₇F = 111.7, ∠HC₂C₁ = 125.3, ∠HC₃C₂ = 118.1, r(C₇-H) = 1.109, r(C₂-H) = 1.086, r(C₃-H) = 1.091, D.M.^a = 2.05 D. ^m∠HC₇F = 109.8, D.M.^a = 2.71 D. ⁿ∠FC₇F = 107.3, ∠HC₂C₁ = 125.4, ∠HC₃C₂ = 118.0, r(C₂-H) = 1.086, r(C₃-H) = 1.092, D.M.^a = 3.25 D. ^o∠ClC₇Cl = 109.6, ∠HC₂C₁ = 125.4, ∠HC₃C₂ = 118.0, ∠(C₂-H) = 1.086, ∠(C₃-H) = 1.091, D.M.^a = 3.29 D. ^pThe dihedral angle defined by the OC₀C₇ atoms and the center of the C₁-C₆ bond is 90°. C₀ refers to the carbonylic carbon. ^q∠HC₇C₀ = 110.8, ∠OC₀C₇ = 124.1, ∠HC₀O = 121.8, ∠H₂C₂C₁ = 125.5, ∠H₃C₃C₂ = 118.0, r(C=O) = 1.220, r(C₀-H) = 1.109, r(C₇-H) = 1.104, r(C₂-H) = 1.086, r(C₃-H) = 1.091, D.M.^a = 2.84 D. ^rThe dihedral angle defined by the OC₀C₇ atoms and the center of the C₁-C₆ bond is 180°. C₀ refers to the carbonylic carbon. ^s∠HC₇C₀ = 115.9, ∠OC₀C₇ = 124.4, ∠HC₀O = 121.4, r(C=O) = 1.206, D.M.^a = 3.72 D. ^tC_N refers to the nitrilic carbon, ∠NCC₇ = 180, ∠C_NC₇A (A = center of the C₁-C₆ bond) = 126.2, ∠H₇C₇C_N = 107.5, ∠HC₂C₁ = 125.5, ∠HC₃C₂ = 118.0, r(C≡N) = 1.161, r(C₂-H) = 1.086, r(C₃-H) = 1.091, r(C₇-H) = 1.104, D.M.^a = 3.03 D. ^u∠NCC₇ = 180, r(C≡N) = 1.139, D.M.^a = 4.44 D. ^vC_N refers to the nitrilic carbon, ∠NCC₇ = 180, ∠C_NC₇C_N = 112.8, ∠HC₂C₁ = 125.3, ∠HC₃C₂ = 119.2, r(C≡N) = 1.160, r(C₂-H) = 1.086, r(C₃-H) = 1.091, D.M.^a = 4.06 D. ^wWith partial geometry optimization at 3-21G* (see footnote d). At 3-21G**/3-21G, the energy is -267.20423.

Ragharachari of various annulenes suggests that HF calculations underestimate bond equalization^{24a} so that in reality the differences in b, c, and d are expected to be even smaller than those calculated at 3-21G*. The small effect of the cyclopropane ring fusion on the vicinal ortho and meta H,H-coupling constants to the size of the fused ring.^{24b,c}

To summarize, the geometry of cyclopropabenzene is not represented correctly by either of the Kekulé structures, **8a** or **8b**. **1** is better represented by a structure containing short a and b bonds and relatively longer c and d bonds. It is interesting to note that Longuet-Higgins and Coulson reached a similar conclusion for hydrindene despite the crudeness of their HMO calculations which included only the π-electrons.¹⁶ However, more recent workers (and to some degree also Longuet-Higgins and Coulson) chose to overlook the changes in all the bond lengths and have focused their attention only on bond a, thus favoring bond localization according to structure **8b**.^{4,16}

It is important to realize that the concept of bond fixation is concerned with localization of electrons in the π-framework, while the geometry is determined by both π- and σ-effects (e.g., strain). It appears that this simple differentiation has not always been stated clearly in the literature, and in some of the previous studies, the bond lengths were assumed to reflect the presence or absence of bond fixation in the π-system (see, however, ref 25). Partially this results from the difficulty to estimate experimentally the degree of localization of the π-electrons.¹⁸ One of the theoretical indexes for probing the degree of bond fixation in the π-framework

is the Mulliken overlap population (MOP) which is related to the bond order.^{26a} The 3-21G MOPs in **1** and the total calculated charges at the carbon atoms are shown in formula 10. For



comparison, the π-overlap population between any two carbon atoms in benzene is 0.293 at 3-21G. The MOPs in **10** point to a small bond localization of the π-electrons in the direction described in **8a**. Thus, the MOPs of bonds b and d are slightly higher, that of bond c is slightly lower, and that of bond a is similar to that in benzene. Sophisticated valence-bond calculations¹² as well as the semiempirical methods give bond fixation in the same direction (i.e., **8a**) but to a larger degree than the above 3-21G calculations (for the CNDO results, see ref 17b; the MINDO/3 and MNDO results are similar). Note that the MOPs points to bond fixation as in **8a**,^{26a,b} while the geometry is more consistent with structure **8b**. We conclude that the bond lengths of **1** (Table I) do not reflect the degree of bond fixation of the π-electrons, and they are therefore a poor guide for evaluating the degree of bond fixation in annelated aromatic systems.

To conclude, the structure of the benzene ring in **1** cannot be understood in terms of π-bond localization. It is preferably in-

(24) (a) Haddon, R. C.; Ragharachari, K. *J. Am. Chem. Soc.* **1985**, *107*, 289. (b) Cooper, M. A.; Manatt, S. L. *Ibid.* **1970**, *92*, 1605. (c) The observation that in **1** J_{meta} (7.63 Hz) > J_{ortho} (6.04 Hz) although d is slightly shorter than c contrasts with the general linear relationship in benzene derivatives between J and CC bond lengths. Other factors associated with the distorted geometry of **1** are probably involved, but an adequate rationalization is not yet available.

(25) Billups, L. E.; Chow, W. Y.; Leavell, K. H.; Lewis, E. S.; Margrave, J. L.; Sass, R. L.; Shiegh, J. J.; Werness, P. G.; Wood, J. L. *J. Am. Chem. Soc.* **1973**, *95*, 7878.

(26) (a) MOPs (or bond orders) are not the best criteria for analyzing the character of conjugated and aromatic systems. More sophisticated analyses, such as "second-order bond fixation" (see: Binsch, G.; Tamir, I. *J. Am. Chem. Soc.* **1969**, *91*, 2450 and references therein) and valence-bond calculations,¹² are available. However, as the MOPs are widely used in discussions of bond fixation, we analyze shortly the calculated values for **1**. (b) The contribution to **1** of ionic resonance structures (in addition to the covalent dominant structures **8a** and **8b**) is small, as indicated by the small polarization of the π-electrons away from the fused cyclopropane ring. Thus, the calculated π-populations (3-21G*, in electrons) are +0.023 at C₁, +0.002 at C₂, and -0.01 at C₃. There is also no electron delocalization from the benzene ring to the cyclopropane ring or vice versa, as indicated by the nearly zero dipole moments (Table I). Similar conclusions were reached in ref 12.

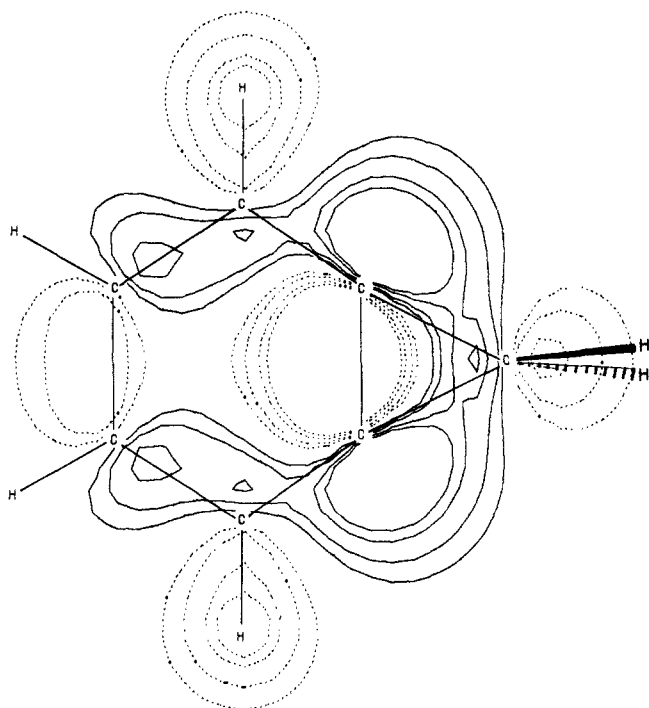
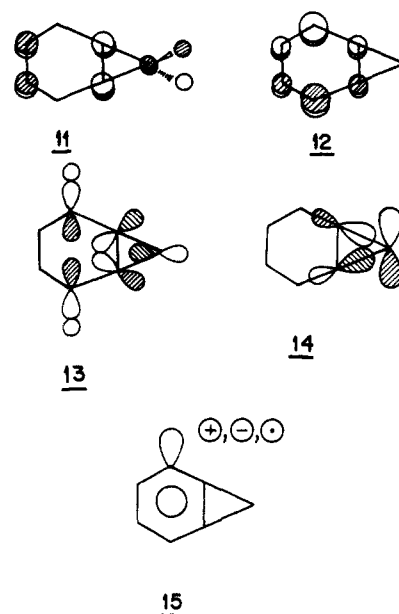


Figure 2. Extended Hückel contour plot in the molecular plane showing the highest σ -type orbital of **1** drawn schematically in **13**. The contour values are 0.2, 0.1, 0.05, and 0.02.

terpreted as reflecting primarily distortions that relieve somewhat the strain associated with the fused cyclopropene ring. These distortions occur mainly around the fusion points; the other parts of the molecule remain essentially unchanged. Thus the bridge bond is shortened by ca. 0.05 Å and the bonds adjacent to the bridge by ca. 0.02 Å relatively to benzene. The bond angles are also strongly distorted in an effort to approach the "normal" external bond angle in cyclopropene of 148.6° (3-21G). Thus α is widened by 4.8° and consequently β shrinks to 113°. The experimental structures of **4–6** reveal similar and even larger distortions. For example, in **4**, $\alpha = 126.6^\circ$, $\beta = 109.3^\circ$, $b = 1.385$ Å, and $c = 1.417$ Å.⁷

c. Reactions of Cyclopropabenzene. The concept of bond fixation was introduced to explain the regioselectivity in the reactions of fused aromatic systems.¹⁴ We will see below that problems arise when this concept is applied to **1**, but that frontier molecular orbital (FMO) theory is useful in discussing its chemistry. The FMO theory concentrates on the energies and charge distributions in the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO, respectively).²⁷ Let us examine these orbitals in **1**. At 3-21G the two highest occupied MOs of **1** are π -type, with the b_1 orbital (see **11**) lying above the a_2 orbital (see **12**). The degeneracy of the a_2 and the b_1 orbitals of benzene is lifted in **1** by interaction with the external C₇-methylene. In **1**, the a_2 orbital is pulled by the inductive effect of the cyclopropene ring to a lower energy relatively to benzene, while the b_1 orbital is pushed to a higher energy (by ca. 0.4 eV) by interaction with the π_{CH_2} orbital (see **11**; note the antibonding relationship between π_{CH_2} and the benzene's b_1 orbital). The highest σ -type orbital (**13**) is of a_1 symmetry but it lies substantially lower in energy. A contour plot of orbital **13** is shown in Figure 2. The calculated orbital ordering, **11** > **12** > **13**, agrees with the interpretation of the photoelectron (PE) spectrum of **1**.²⁸ The quantitative agreement between the calculations and the PE spectrum is also reasonable. At 3-21G the energies of the b_1 and the a_2 orbitals are -8.87 and -9.41 eV, respectively, compared with -8.82 and -9.48 eV, respectively, according to the PE



spectrum (using the Koopmans theorem²⁹).²⁸ The calculated energy of the highest σ -orbital **13** is, however, too low (-11.51 eV at 3-21G compared with the experimental ionization energy of 10.17 eV).²⁸ Cyclopropene exhibits a similar behavior. The agreement between the vertical ionization potentials (IP)³⁰ and the 3-21G calculations is excellent for the π -orbital (9.82 and 9.85 eV, respectively), but the energy of the $3b_2$ σ -orbital is too low at 3-21G (-11.37, -10.95 eV experimentally^{29,30}).

Another point of interest is the reversal in the order of the Walsh σ -orbitals in **1** compared with cyclopropene or 1,2-dimethylcyclopropene. In cyclopropene the a_1 orbital (i.e., analogous to **13**) is substantially lower in energy than the anti symmetric b_2 Walsh orbital (i.e., analogous to **14**). The calculated vertical ionization potentials are 13.52 and 11.37 eV at 3-21G compared with 12.59 and 10.95 eV experimentally.³⁰ In 1,2-dimethylcyclopropene both orbitals are pushed up in energy relative to cyclopropene by the in-plane interactions with the $\sigma(\text{C}-\text{CH}_3)$ -bonds (the calculated 3-21G IPs (in eV) are 12.27 (a_1), 10.64 (b_2), 8.98 (π); no experimental data are available for comparison). Bending of the external methyl groups lowers the energy of the b_2 orbital and raises the energy of the a_1 orbital. The energies of the two orbitals are nearly equal at a H₃C-C=C angle of ca. 130°, and at smaller angles the a_1 orbital lies above the b_2 orbital. This is the orbital ordering in **1** where $\alpha = 124.8^\circ$; the calculated IPs (3-21G) are 11.51 eV for the a_1 orbital and 12.33 eV for the b_2 orbital. The reversal in the ordering of the a_1 - b_2 pair may be significant in systems such as **3**^{5b,c} or **15**³¹ in which interactions within the σ -framework are expected to dominate the stability and the reactions of these species.

Experiment and theory agree that there is a substantial energy gap between the π - and σ -orbitals of **1**. Thus, within the FMO theory framework, the reactions of cyclopropabenzene are expected to be dominated mainly by the π -orbitals. Cyclopropabenzene having a higher HOMO is expected to be more reactive in reactions with electrophiles than benzene. Unfortunately, such reactions always lead to cleavage of the three-membered ring and not to aromatic substitutions,⁴ so that the rates of aromatic substitution of **1** and of benzene cannot be directly compared. The HOMO of **1**, orbital **11**, is localized at the fused bond (C₁-C₆) and at the C₃-C₄ bond. The a_2 orbital, orbital **12**, lies 0.54 eV lower in energy, and its highest coefficients are at C₂ and C₅. According to FMO theory, electrophilic attack should therefore occur preferably at the fused bond. Is this prediction correct?

(29) Koopmans, T. *Physica* 1934, 1, 104.

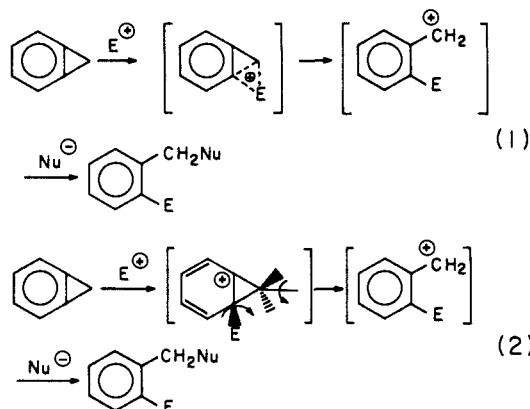
(30) (a) Bieri, G.; Burger, F.; Heilbronner, E.; Maier, J. P. *Helv. Chim. Acta* 1977, 60, 2213. (b) Gleiter, R. *Top. Curr. Chem.* 1979, 86, 197.

(31) Apeloig, Y.; Arad, D. *J. Am. Chem. Soc.* 1985, 107, 5285 and unpublished data.

(27) Fleming, I. In *Frontier Orbitals and Organic Chemical Reactions*; Wiley: New York, 1976.

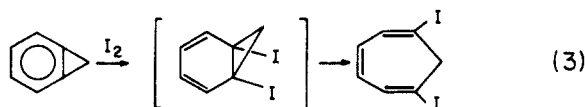
(28) Brogli, F.; Giovannini, E.; Heilbronner, E.; Schurter, R. *Chem. Ber.* 1973, 106, 961.

Reactions of **1** with electrophiles result in cleavage of the cyclopropene ring. The products in most of these reactions can be rationalized by an electrophilic attack at the strained σ -bond followed by ring cleavage and a nucleophilic capture of the resulting benzyl cation (eq 1).^{4,32} If this is indeed the operative mechanism, then the cleavage products provide no information regarding the site of electrophilic attack at the π -system. The



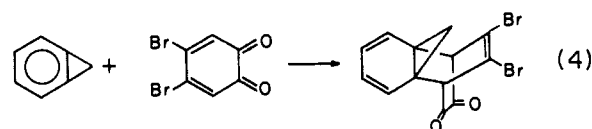
calculations and in particular the large π - σ -splitting argue, however, for the operation of a "normal" aromatic electrophilic substitution mechanism, in which the electrophile attacks first the π -system at either C_1 or C_6 (eq 2). The attachment of the electrophile to either C_1 or C_6 is expected to be extremely facile because it can be accompanied by a synchronous "symmetry-allowed" disrotatory ring opening³³ that relieves most of the strain in **1**. Cyclopropabenzene indeed reacts with electrophiles extremely fast in comparison to benzene and other aromatic systems.^{4,34}

There are yet no clear-cut experiments that differentiate between the mechanisms of eq 1 and 2. We know of at least one electrophilic reaction (eq 3) which is consistent with the mechanism in eq 2 but which is difficult to rationalize according to the mechanism in eq 1 (even in this reaction, the ring cleavage products dominate and only 6% of 1,6-diiodocycloheptatriene is produced).³⁵



Garratt et al. who analyzed the addition products of various electrophiles (bromine, iodine, and HCl) to 2-methylcyclopropabenzene concluded that these reactions proceed via the mechanism of eq 2 in agreement with the FMO analysis, while reactions in the presence of silver salts proceed via the mechanism of eq 1.³⁶ Additional studies, both theoretical and experimental, are needed in order to differentiate between the mechanisms of eq 1 and 2. Such studies are in progress in our laboratory.³⁴

Cyclopropabenzene undergoes cycloaddition reactions with a variety of dienes, mostly electron-poor (the reaction with butadiene itself is slow and probably proceeds through diradical intermediates).^{4,37} These reactions belong to the category of cycloadditions with "inverse electron demand", in which the dienophile is the electron donor and the diene is the electron acceptor.^{27,38} One example is the addition of **1** to 4,5-dibromo-*o*-benzoquinone (eq 4). Note that cycloaddition across bond *a* can be ration-



alized³³ either as a symmetry-allowed [6s + 4s] process for **8a** or as a [2s + 4s] process for **8b**. Experiments which may clearly differentiate between these alternative mechanisms (e.g., by determining if the products arise from endo or exo cycloaddition) are not yet available. However, as **1** reacts as an electron-rich dienophile, its HOMO **11** is expected to play the major role in these cycloaddition reactions.²⁷ Orbital **12** is suitable for acting as the 2s component in the cycloaddition reaction. Orbital **12** which can participate as the 6s component is lower in energy and therefore interacts less effectively with the diene's LUMO. Thus, the FMO analysis favors a [2s + 4s] process of **8b** rather than a [6s + 4s] process of **8a**.³⁹

In conclusion, the chemistry of **1** is nicely rationalized by FMO theory. We wish to point out that the concept of bond fixation was originally introduced to explain the regioselectivity in the reactions of fused aromatic systems.¹⁴ According to this concept and assuming that other factors are unimportant, bond fixation as in **8a** (which reflects the π -distribution and the valence-bond picture of HOD¹²) suggests that **1** would be attacked by electrophiles at C_3 (C_4) or at C_2 (C_5) and that it would react as diene in cycloadditions. On the other hand, if structure **8b** predominates, **1** is expected to act as a dienophile in cycloadditions and react with electrophiles at C_1 or C_6 . The chemistry of **1** as described above seems to be more consistent with structure **8b**. Thus, if the relative weights of Kekulé structures are indeed reflected in the chemistry of **1** as Miles and Nixon have argued,¹⁴ then the experimental evidence can be interpreted as requiring a larger contribution of structure **8b** than of **8a**. Of course, it is possible that structure **8a** predominates (as HOD find¹²), yet the reactions of **1** are dictated by a combination of several factors such as the net charges, orbital interactions, and bond fixation.

Finally, a general comment regarding the concept of "bond fixation" is in order. HOD concluded in their recent valence-bond study that bond fixation is important in both **1** and cyclobutabenzene.¹² Although the HOD analysis is theoretically superior to ours, we wish to point out that the above discussion reveals that the concept of bond fixation, even if it is valid,¹⁸ is of little practical merit. Bond fixation according to **8a**, as HOD find,¹² does not describe correctly the geometry of **1** nor does it help in analyzing its reactions (the same applies to the π -overlap populations). A deeper insight into the chemistry of **1** is gained by FMO analysis. Therefore, until new supportive experimental evidence is presented (e.g., see ref 18), or until the properties of **1** are rationalized in terms of structure **8a**, we see little advantage in discussing **1** and related systems in terms of the Miles-Nixon effect,¹⁴ although this concept may be theoretically valid.

d. Strain Energy. The strain energy of cyclopropabenzene is of special interest. It has been determined experimentally as 68 kcal·mol⁻¹ from the heats of silver ion catalyzed methanolysis reactions.²⁵ This value is significantly higher than the total strain energy of cyclopropene which is 52.6 kcal·mol⁻¹.⁴⁰ The 15.4 kcal·mol⁻¹ difference between these values reflects the additional strain that results from the distortive fusion of the benzene and the cyclopropene rings. It is important to determine if theory can reproduce the experimental strain energy of **1**. If this is so, then one can use theory confidently to calculate the strain energies of other annelated aromatics (such as **2** or **3**), where experimental values are not available.

(32) For an excellent analysis of the mechanism of electrophilic cleavage of cyclopropanes and fused "saturated" cyclopropanes, see: Wiberg, K. B.; Kass, S. R.; de Meijere, A.; Bishop, K. C. *J. Am. Chem. Soc.* **1985**, *107*, 1003. And preceding papers (i.e., *Ibid.*, **1985**, *107*, 996, 988.).

(33) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*, Verlag Chemie: Weinheim, Germany, 1971.

(34) 2-Methoxycyclopropabenzene reacts with various electrophiles instantaneously at room temperature: Arad, D. Ph.D. Thesis, Technion, Israel, 1986.

(35) Vogel, E.; Grimme, W.; Korte, S. *Tetrahedron Lett.* **1965**, 3625.

(36) Bee, L. K.; Garratt, P. J.; Mansuri, M. M. *J. Am. Chem. Soc.* **1980**, *102*, 7076.

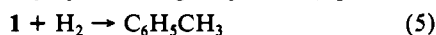
(37) For more recent examples, see: (a) Martin, J. C.; Muchowski, J. M. *J. Org. Chem.* **1984**, *49*, 1040. (b) Kato, H.; Toda, S. *J. Chem. Soc., Chem. Commun.* **1982**, 510.

(38) Sauer, J.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 779.

(39) Cycloadditions with "normal electron demand", i.e., with electron-rich dienes, do not contribute to differentiating between structures **8a** and **8b**, because in these reactions the LUMO of **1** plays the decisive role and information about the charge-distribution in **1** is not obtained.

(40) Wiberg, K. B.; Fenoglio, R. A. *J. Am. Chem. Soc.* **1968**, *90*, 3395.

The most direct and widely used reaction for determining strain energies is hydrogenation (e.g., eq 5). The strain of **1** was determined experimentally by an analogous process (eq 6).²⁵



At either STO-3G, 3-21G, or 3-21G*, the calculated energies of eq 5 and 6 are in poor agreement with experiment (see below). This failure is to be expected at this level of theory because eq 5 and 6 are not isodesmic; i.e., the types and number of bonds on the two sides of the equations are different.⁴¹ It is well established that an accurate estimate of nonisodesmic equations can be obtained only if electron correlation is included in the calculations.⁴² As **1** is a relatively large molecule, our calculations do not include correlation energy, and for estimating correctly the strain in **1**, it is therefore essential to use isodesmic equations^{41,42} such as eq 7. Equation 7 compares the energies of the ring-cleaving hydrogenations of **1** and of cyclopropene (i.e., it is obtained by subtracting eq 5 from an analogous equation for cyclopropene).



The calculated energies of eq 7 are $-19.7 \text{ kcal}\cdot\text{mol}^{-1}$ at STO-3G, $-15.7 \text{ kcal}\cdot\text{mol}^{-1}$ at 3-21G, $-17.6 \text{ kcal}\cdot\text{mol}^{-1}$ at 3-21G*/3-21G,⁴³ and $-12.9 \text{ kcal}\cdot\text{mol}^{-1}$ according to MNDO. As expected for an isodesmic equation,⁴² the energies of eq 7 are not very sensitive to the basis set that is used. Equation 7 measures the additional strain that results from the fusion of benzene and cyclopropene, and the theoretical estimate of $16\text{--}18 \text{ kcal}\cdot\text{mol}^{-1}$ is in excellent agreement with the experimental value of $15.4 \text{ kcal}\cdot\text{mol}^{-1}$.²⁵ The MNDO value is also close to the experimental value.

The heat of formation of cyclopropabenzene (in the gas phase) can be evaluated from the calculated energy of eq 7 and the known heats of formations of propene, toluene, and cyclopropene.⁴⁴ Thus, $\Delta H_f^\circ(\mathbf{1}) = 66.2 + 12.0 - 4.9 + 17.6 (3\text{-}21\text{G}^*) = 90.9 \text{ kcal}\cdot\text{mol}^{-1}$. The $\Delta H_f^\circ(\mathbf{1})$ calculated with MNDO is similar; i.e., $89.7 \text{ kcal}\cdot\text{mol}^{-1}$. The energy of the ring-cleaving hydrogenation of **1** (eq 5) which could not be calculated directly with acceptable accuracy can be now estimated from the experimental ΔH_f° of toluene⁴⁴ and the theoretical ΔH_f° of **1** as $12.0 - 90.9 = -78.9 \text{ kcal}\cdot\text{mol}^{-1}$. As expected,^{41,42} this value is considerably lower than the calculated energies of eq 5 at either 3-21G ($-103.0 \text{ kcal}\cdot\text{mol}^{-1}$) or at 3-21G* ($-93.5 \text{ kcal}\cdot\text{mol}^{-1}$). Wiberg has found that 6-31G*

hydrogenation energies of various olefins are generally too high by $11\text{--}15 \text{ kcal}\cdot\text{mol}^{-1}$.⁴⁵ Applying this correction for the effect of correlation energy to the 3-21G* energy of eq 5 yields a heat of hydrogenation of ca. $80 \text{ kcal}\cdot\text{mol}^{-1}$, in agreement with the above indirect estimate of $-78.9 \text{ kcal}\cdot\text{mol}^{-1}$. For predicting the experimental heat of hydrogenation of **1**, the calculated energy of eq 5 must be corrected for zero-point energy (ZPE) changes and for the changes in ΔH_f° in going from 0 to 298 K. We apply an average correction obtained from a series of olefins,⁴⁵ i.e., $\Delta\text{ZPE} = 8.2 \text{ kcal}\cdot\text{mol}^{-1}$ and $\Delta\Delta H_f^\circ = -1.8 \text{ kcal}\cdot\text{mol}^{-1}$, to calculate that in the gas phase, the heat of hydrogenation of **1** (eq 5) is $-78.9 + 8.2 - 1.8 = -72.5 \text{ kcal}\cdot\text{mol}^{-1}$. This prediction awaits experimental testing.

The good agreement that we find between the calculated and the experimental strain energies of **1**, using either the semiempirical or the ab initio methods, suggests that one can extend such studies with some confidence to other cycloproparenes.

Conclusions

Several conclusions emerge from this study: (1) Fusion of cyclopropene and benzene results in severe geometrical distortions, mainly around the bridge carbons. However, these distortions do not reflect the π -charge distributions. (2) The degree of π -bond fixation (as derived from the Mulliken π -overlap populations) is very small. (3) The chemistry of cyclopropabenzene is effectively rationalized by FMO theory as being dominated by its HOMO and the possibility of considerable relief of strain by ring cleavage. The HOMO of cyclopropabenzene is localized at the bridge carbons which are therefore the preferred sites for reactions with electrophiles and electron-poor dienes. (4) The concept of bond fixation provides no help in understanding either the geometry or the chemistry of cyclopropabenzene. (5) The reasonable agreement between the 3-21G (and even STO-3G) calculations and experiment, for both the geometry and the strain energy of **1**, is encouraging and suggests that similar calculations can be applied *predictively* to related systems where experimental data are missing. Studies along this line (e.g., for **2**, **3**,^{5c} and cyclopropanaphthalene) are in progress in our laboratory. The semiempirical methods (e.g., MINDO/3 and MNDO) give erroneous results for the geometry, but the agreement for ΔH_f° is good. Semiempirical methods should be therefore applied to related molecules only with extreme caution, especially for the evaluation of geometry.

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(43) Partial geometry optimization at 3-21G* lowers the energy of **1** by only $0.3 \text{ kcal}\cdot\text{mol}^{-1}$ (Table I) so that the 3-21G*/3-21G* and the 3-21G*/3-21G energies of eq 7 are expected to be similar.

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