Table I. Conformational Energy Barriers in Cyclic Ketones, $(CH_2)_{n-1}C{=}O$

	$\Delta G^{\ddagger}$, kcal/mol[a]	
Ring size (n)	Cmr spectrum	Pmr spectrum
6		4.0[b]
8		6.3 and 7.5[c]
9	5.0	5.0 and 6.5
10	6.6	6.5 and 7.3
11	5.7	6.0 and 6.9
12	7.3	*ca.* 7.6
13	*ca.* 5.8	*ca.* 5.6
14	*ca.* 5.9	*ca.* 6.3 and *ca.* 6.7
15	*ca.* 5.0	*ca.* 5.0
16	*ca.* 5.5	*ca.* 5.6

[a] Errors in $\Delta G^{\ddagger}$ are estimated to be ±0.2 kcal/mol, except where approximate values are given when the errors may be up to ±0.4 kcal/mol. [b] F. A. L. Anet, G. N. Chmurny, and J. Krane, *J. Amer. Chem. Soc.*, **95**, 4423 (1973). [c] F. A. L. Anet, M. St. Jacques, and P. M. Henrichs, *Intra-Sci. Chem. Rep.*, **4**, 251 (1970).

the C_{10} ketone. In cyclotridecanone, the α-carbon resonance is a narrowly spaced doublet at low temperatures, but the other methylene carbons are so overlapped that it is difficult to be certain that there is only one kind of conformation. The cmr spectra of cyclotetradecanone reveal the presence of at least two different kinds of conformations. At −160°, there are two carbonyl bands (intensity ratio 3:2) separated by 1.3 ppm, and the α-carbon resonance is complex. The C_{15} and C_{16} ketones also show evidence for more than one kind of conformation, since the α-carbon resonances in both compounds are ill-defined at low temperatures.

Although the precise conformations of the C_9, C_{11}, C_{13}, C_{14}, C_{15}, and C_{16} ketones remain unclear, a definite conformation can be assigned to the C_{12} ketone. There is strong evidence that cyclododecane exists virtually exclusively in the "square" (D_4) conformation.[2b,9] It appears very likely that the C_{12} ketone has the same ring skeleton as the parent hydrocarbon; symmetry then requires that the carbonyl group be in the noncorner position (I) as would be expected.[7]

Approximate free energy barriers obtained from the cmr spectra of the C_9–C_{16} cyclic ketones are given in Table I.

The 251-MHz pmr spectra of the cycloalkanones discussed above are very complicated at low temperatures, but changes in the α- and β-proton resonances can be interpreted in some cases. In cyclodecanone, the α-protons give rise to four chemical shifts (δ 2.04, 2.15, 2.52, 3.41 ppm) at −160°, as expected from the unsymmetrical BCB-3 conformation. Two distinct averaging processes (Table I) are visible as the four α-proton bands change first to two bands (δ *ca.* 2.3 and 2.4) at *ca.* −125° and then to one band above *ca.* −112°. Similar changes are observed for the β protons in cyclodecanone-$\alpha,\alpha,\alpha',\alpha'$-$d_4$.

The lower energy process in cyclodecanone corresponds to that observed in the cmr spectrum (Table I) and is probably a pseudorotation of the BCB-3 *via* the BCB-6 to the mirror image BCB-9. In this process the carbonyl group remains in a favorable site for relieving nonbonded interactions. In order to average the four α-proton resonances of cyclodecanone into one resonance, additional pseudorotation cycles are needed, *e.g.*, BCB-3 → BCB-10 → BCB-7 → BCB-4, and this requires a higher energy, particularly for the BCB-10 to BCB-7 step, as the carbonyl group is forced to remain in the unfavorable corner position during this process.

Cyclododecanone has four α-proton resonances at low temperatures but, in contrast to the C_{10} ketone, these bands coalesce at higher temperatures to a single resonance without passing through a distinct two-resonance region. Two different processes can be envisaged here as in cyclodecanone, but the free energies of activation must be closely comparable. This is reasonable, as nonbonded interactions in the C_{12} ketone should be very much weaker than in the C_{10} ketone.

Two distinct processes can be observed in the pmr spectra of cyclononanone and cycloundecanone (Table I), but in the C_{13}, C_{14}, C_{15}, and C_{16} ketones the spectral changes are too complex for unambiguous interpretation. Nevertheless, approximate $\Delta G^{\ddagger}$'s (Table I) can be obtained. Any process observed in the carbon spectrum must be visible (in the absence of many coincidences) in the proton spectrum, and the data in Table I are in agreement with this requirement.

Highly deuterated as well as ^{13}C enriched derivatives of the C_9–C_{16} ketones are being synthesized in order to obtain simpler low-temperature nmr spectra. As shown in Table I, all the cycloalkanones from C_6 to C_{16} have conformational barriers ≥4 kcal/mol, with the exception of cycloheptanone, which is expected to have a barrier too low for nmr measurement.[8,10]

Acknowledgments. We thank Dr. J. J. Wagner for preliminary measurements on the C_9 and C_{10} ketones, Dr. T. Ledaal, University of Oslo, and Drs. A. F. Thomas and K. H. Schulte-Elte of Firmenich, Geneva, for gifts of large-ring ketones, and the National Science Foundation for financial support.

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(10) G. Borgen and J. Dale, *Acta Chem. Scand.*, **26**, 3593 (1972).

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Structure and Thermochemistry of Benzocyclopropenes. The Question of Bond Fixation and Strain Energy

Sir:

Although benzocyclopropene (**1**),[1] naphtho[*b*]cyclopropene (**2**),[2] and several of their derivatives[3] have been reported, the important questions of bond fixation and strain associated with these systems remain largely unanswered.[4] We report here the crystal structure of **2** and the thermochemistry of **1** and **2**.

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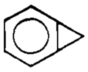
(1) (a) E. Vogel, W. Grimme, and S. Korte, *Tetrahedron Lett.*, 3625 (1965); (b) W. E. Billups, A. J. Blakeney, and W. Y. Chow, *Chem. Commun.*, 1461 (1971).

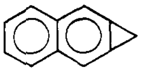
(2) W. E. Billups and W. Y. Chow, *J. Amer. Chem. Soc.*, **95**, 4099 (1973).

(3) For a comprehensive review see: B. Halton, *Chem. Rev.*, 73, 113 (1973).

(4) An X-ray crystallographic structural analysis of a substituted benzocyclopropene has now appeared. See E. Carstensen-Oeser, B. Muller, and H. Durr, *Angew. Chem.*, **84**, 434 (1972); *Angew. Chem., Int. Ed. Engl.*, **11**, 422 (1972), and relevant references therein.



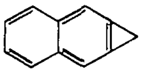
1



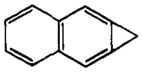
2

The molecular dimensions of **2** were determined by single-crystal X-ray diffraction analysis. Bond distances and angles are shown in Figure 1.[5,6]

In terms of the structure of Figure 1, although "fixation" of double bonds in the 1,2 and 3,4 positions seems initially satisfactory since they are substantially shorter than the corresponding bonds in naphthalene, a problem arises from the presence of three adjacent short bonds (1,2, 1.337; 2,3, 1.368; 3,4, 1.337) which is not reconcilable with any scheme in which bond shortening is due to contributions of double bond character since all three cannot have more double bond character than the bonds in benzene. The structure of dimethyl 1,4-diphenylbenzocyclopropene-7,7-dicarboxylate[4] shows the same anomaly differing from the present case mainly by the extreme shortening (1.333 Å) of the bridging bond.[7] The relation between structure and resonance in terms of "bond fixation" has been discussed for these systems in the review by Halton,[3] and the conclusions were then ambiguous. The present structure does not resolve any difficulties, since there is no evidence for bond localization in the direction of either mesomeric limiting structure **2a** or **2b**.[9,10]



2a



2b

To determine the amount of strain energy associated with **1** (estimated to be 45 kcal mol^{-1} greater than that of cyclopropane[11]), the Ag(I) catalyzed methanolysis[2] was employed. This reaction is fast and quantitatively furnishes benzyl methyl ether. Thus, the enthalpy change for the transformation **1** (liquid) + CH_3OH (liquid) → ether (solution) was determined as −49.4 ± 0.2 kcal mol^{-1} at 25°.[12] This value was derived from the data in Table I by correcting for the 5% of unreactive impurities present in benzocyclopropene.[13] Adjusting this value for the heat of solution of benzyl methyl ether in methanol (0.70 ± 0.02 kcal mol^{-1}) gives −51.1 kcal mol^{-1} for the heat of reaction with all components in the liquid state.

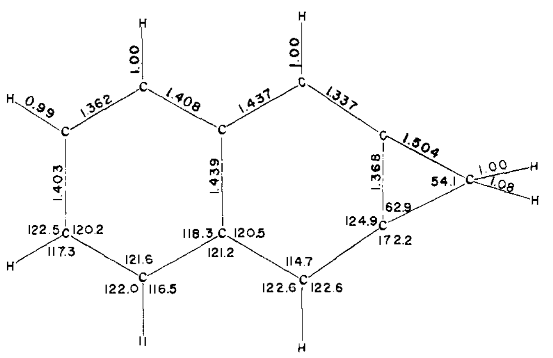


Figure 1. Bond lengths and angles of naphtho[*b*]cyclopropene. The two halves of the molecule are crystallographically equivalent across a mirror plane perpendicular to the *b* axis of the unit cell. Estimated standard deviations are 0.004–0.006 Å for C–C bonds, 0.04–0.06 Å for C–H bonds, 0.3° for C–C–C bond angles, and 2° for C–C–H bond angles. No dimensional corrections for vibrational parameters were made. All carbon atoms are within ±0.01 Å of a common least-squares plane. The calculated angle between the plane of the three-membered ring and the plane of the remainder of the molecule is 0.7 ± 0.5°.

Table I. Enthalpy Change for the Reaction **1** (liquid) + CH_3OH (liquid) → ether (solution)[a]

Run	Benzocyclopropene, g	ΔH, kcal mol^{-1}
1	0.3724	−46.8
2	0.2526	−47.1

[a] Anhydrous reagent grade methanol (225 ml) was used.

To evaluate the amount of strain energy present in benzocyclopropene it is necessary to compare the experimentally determined heat of formation with a value that one would expect from a strain-free model. Unfortunately, the heat of formation of the product benzyl methyl ether has never been measured, and approximations, therefore, have to be made to ascertain these quantities. The calculation was carried out as follows.

From Franklin's group equivalents[14] the gas-phase heats of formation for benzocyclopropene[15] and benzyl methyl ether[16] can be calculated at 25°. These values are +19.07 and −20.25 kcal mol^{-1}, respectively. To extend these values to the liquid phase, the heats of vaporization must be subtracted. The heats of vaporization of benzocyclopropene were assumed to be between those of benzene and toluene (103.6 and 98.5 cal/g at 25°).[17] The xylene isomers also have heats of vaporization around 100 cal/g.[17] Therefore, the heat of vaporization of benzocyclopropene is approximately 9.0 kcal mol^{-1}. The heat of vaporization of benzyl

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[5] The data were obtained using an automatic diffractometer. The crystals are orthorhombic (D_{2h}^{16}-*Pnma*) with a = 11.391, b = 10.398, and c = 6.390 Å. There are four molecules per unit cell. The crystal chosen for data collection was needle shaped (0.3 × 0.3 × 2.0 mm). Several reference reflections were monitored throughout the data collection and showed less than 1% change in intensity. Trial parameters for all carbon atoms were deduced from a three-dimensional Patterson synthesis. Hydrogen atoms were found by a Fourier difference synthesis after preliminary isotropic least-squares refinement. Final parameters were obtained from an anisotropic least-squares refinement on 540 observed reflections; the R value equals 5.8%. No anomalies such as excessively large or otherwise unrealistic temperature factors were encountered during refinement.

[6] See paragraph at end of paper regarding supplementary material.

[7] It is tempting to attribute the difference in this bond length in the two cases to an effect of the carboxylate groups, analogous to the effect of two cyano groups which stabilize the norcaradiene structure relative to the cycloheptatriene structure, both effects apparently leading to a shortening of the distance between the β carbons.[8]

[8] E. Ciganek, *J. Amer. Chem. Soc.*, **89**, 1454 (1967).

[9] Recent calculations[10] employing the CNDO/2 semiempirical molecular orbital method predict an increase in the length of the bridging bond in benzocyclopropene, in contrast to the experimentally determined values reported here and elsewhere.[4]

[10] C. S. Cheung, M. A. Cooper, and S. L. Manatt, *Tetrahedron*, **27**, 701 (1971).

[11] E. F. Ullman and E. Buncel, *J. Amer. Chem. Soc.*, **85**, 2106 (1963).

[12] The calorimeter employed in this work has been described previously: R. B. Turner, W. R. Meador, and R. E. Winkler, *J. Amer. Chem. Soc.*, **79**, 4116 (1957).

[13] The major impurities are styrene and toluene which are present in the synthetic material. The amounts were determined by glpc analysis of the products after complete reaction of a benzocyclopropene sample.

[14] J. L. Franklin, *Ind. Eng. Chem.*, **41**, 1070 (1949); *J. Chem. Phys.*, **21**, 2029 (1953).

[15] The sum of the Franklin group equivalents for benzocyclopropene is 24 kcal mol^{-1} (ortho disubstituted benzene) − 4.93 kcal mol^{-1} ($-CH_2-$) = +19.07 kcal mol^{-1}.

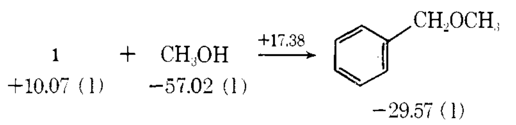
[16] For benzyl methyl ether +22 (monosubstituted benzene) − 4.93 ($-CH_2-$) − 27.2 ($-O-$) − 10.12 ($-CH_3$) = −20.25 kcal mol^{-1}.

[17] J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier, New York, N. Y., 1950.

methyl ether was calculated from its boiling point using Trouton's rule as ~9.3 kcal mol^{-1}.

Alternatively, by the Laidler process[18] using for benzocyclopropene $6E(C_b–C_b) + 4E(C_b–H) + 2E(C_b–C) + 2E(C–H)_s$, one obtains $\Delta H_f(g) = +19.46$ kcal mol^{-1}. Similarly, benzyl methyl ether with $6E(C_b–C) + 5E(C_b–H) + 1(C_b–C) + 2E(C–H)_s{}^\circ + 2E(C–O) + 3E(C–H)_p{}^\circ$ yields $\Delta H_f(g) = -19.79$ kcal mol^{-1}.

Thus, for the unstrained model, we can calculate a heat of reaction in solution of +17.38 kcal mol^{-1} by Franklin's method or +17.47 by the Laidler method. Since the observed reaction heat is 51.1 ± 0.2 kcal mol^{-1}, the disparity must be due to the strain present in the system. *This strain is apparently 68 kcal mol^{-1}!* This value is substantially greater than the total strain energy of 52.6 kcal mol^{-1} found for cyclopropene[19] and is comparable to the total strain energy of the bicyclobutane system for which a strain of 68.2 kcal mol^{-1} was found for 1,3-dimethylbicyclo[1.1.0]butane.[20] This high strain energy doubtless accounts for the extremely high reactivity of this compound.



In a similar manner the heat of methanolysis of **2** was determined, and the data are shown in Table II.

Table II. Enthalpy Change for the Reaction **2** (solid) + CH_3OH (liquid) → ether (solution)

Run	Naphtho[*b*]-cyclopropene, g	ΔH, kcal mol^{-1}
1	0.2227	−47.55
2	0.1926	−47.32

By the Laidler scheme, the gas-phase heat of formation of **2** is +36.23 kcal mol^{-1} and −13.14 for the methanolysis product. Assuming a heat of vaporization of 18 kcal mol^{-1} for **2** and 12 kcal mol^{-1} for the ether, the calculated heat of reaction is +13.65 kcal mol^{-1}. Correcting the observed heat of reaction (47.43 kcal mol^{-1}) for the heat of solution of **2** (assumed to be 4–5 kcal mol^{-1}) and the heat of solution of the ether (about 0.7 kcal mol^{-1}) gives the estimated heat of reaction of all components in the liquid phase as −52 to −53 kcal mol^{-1}. This results in a strain energy of 65–67 kcal mol^{-1}.

It was of interest to compare this value with one obtained from more reliable combustion data. Five determinations of the heat of combustion of **2** yielded a value of $\Delta H_c{}^\circ = -1393.8 \pm 0.2$ kcal mol^{-1}. The derived heat of formation of solid **2** is then +86.0 ± 0.2 kcal mol^{-1} and the heat of formation of gaseous **2** becomes[21] +104 kcal mol^{-1}. Comparing this with the value of 36.2 kcal mol^{-1} predicted from the Laidler scheme yields a strain energy of 67.8 kcal mol^{-1}, in good agreement with the value obtained from the methanolysis of **2** and not appreciably different from that found for **1**.

Finally, it should be noted that the thermal data provide information regarding the difference between the real substance and a model. Such differences are often called strain energies or resonance energies, depending on the sign. In the present case where there is clearly some strain, and the aromatic system is deformed, it would not be reasonable to ascribe the effect exclusively to loss of strain or resonance energy. The strain energy of **1** is 68 kcal mol^{-1} if the resonance energy is the same as that of benzene, and, similarly, the strain energy of **2** is 67.8 kcal mol^{-1}, if the resonance energy is the same as that of naphthalene.

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Supplementary Material Available. A listing of structure factor amplitudes, positional parameters, and temperature factors will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-73-7878.

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[18] J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, New York, N. Y., 1970, p 592.

[19] K. B. Wiberg and R. A. Fenoglio, *J. Amer. Chem. Soc.*, **90**, 3395 (1968).

[20] R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, Jr., and M. Pomerantz, *J. Amer. Chem. Soc.*, **90**, 4315 (1968).

[21] The heat of vaporization of **2** was estimated as 18 kcal mol^{-1}, similar to that of naphthalene.

[22] Alfred P. Sloan Foundation Fellow, 1973–1975.

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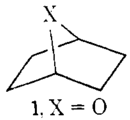
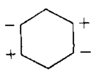
Photoelectron Spectrum of 7-Thiabicyclo[2.2.1]heptane

Sir:

We have recently found that the highest occupied level, which is the oxygen lone pair, of both tetrahydrofuran and 7-oxabicyclo[2.2.1]heptane (**1**) has the same ionization potential (IP = 9.57 eV).[1] This, together with the lack of appreciable interaction between the n_O and π_{CC} levels in 7-oxabicyclo[2.2.1]hept-2-ene, leads to the conclusion that the n_O orbital of **1** is unusually localized. Very recently Hoffmann, *et al.*, have suggested that the highest occupied σ orbital in boat cyclohexane has the symmetry shown in **2**.[2] This σ level is thus unable to interact with the n_O level in **1**,



1, X = O
3, X = S



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[1] A. D. Bain, J. C. Bünzli, D. C. Frost, and L. Weiler, *J. Amer. Chem. Soc.*, **95**, 291 (1973).

[2] R. Hoffmann, P. D. Mollère, and E. Heilbronner, *J. Amer. Chem. Soc.*, **95**, 4860 (1973).