36736-67-1; **18,** 36736-68-2; **19,** 36736-69-3; **19** DNP, 36736-70-6; **20,** 36736-71-7; **21a,** 36736-72-8; *syn*-**21b,** 36744-46-4; *anti*-**21b,** 36744-47-5; **22,** 36736-73-9; **22** DNP, 36736-74-0; **22** (13-hydroxymethylene derivative), 36736-75-1; **22** (13-$COCOOCH_3$ derivative), 36736-76-2; **23** DNP, 36736-77-3; **24a,** 36736-78-4; **24b,** 36736-79-5; **24c,** 36736-80-6; **25a,** 36736-81-9; **25b,** 36736-82-0; **25d,** 36736-83-1; **25f,** 36736-84-2; **26a** HCl, 36736-85-3; **26b** picrate, 36736-86-4; **26c,** 36736-87-5; **26d** HCl, 36736-88-6; **26e** HI, 36736-89-7; **26e** HCl, 36736-90-0; **26f** HCl, 36736-91-1; 10-bromo-5-chloro-5*H*-dibenzo[*a,d*]cycloheptene, 36736-92-2; 5-(10-bromodibenzo[*a,d*]cycloheptenyl)acetic acid, 36736-93-3; diethyl 5-(10-cyano-5*H*-dibenzo[*a,d*]cycloheptenyl)malonate, 36736-94-4; 5-(10-carboxamide-5*H*-dibenzo[*a,d*]cycloheptenyl)malonic acid, 36736-95-5; 5,10-ethano-10,11-dihydro-5*H*-dibenzo[*a,d*]-cyclohepten-12-ol, 36736-96-6.

Acknowledgment.—We are indebted to Mr. George Robertson and Mr. Rudolf Oeckinghaus for microanalytical data, to Miss Natalie Cahoon, Mr. Mike Hotalski, Mr. Charles Navarro, and Mr. Anis Hamden for spectra, to Mr. Robert Dziemian, Miss Ann Smith, and Mr. Hassan Haider for large-scale preparation of intermediate **18**, and to Miss Ruth Behnke for nmr spectra. A few of the early experiments (Scheme I) were carried out by Mr. Robert J. Kempton.

Hybridization in Fused Strained Rings by the Maximum Overlap Method. II. Benzocyclobutene and Benzocyclopropene[1a]

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The hybridization in benzocyclobutene and benzocyclopropene is considered using the method of maximum overlap. The results show considerable variations of s–p content of hybrids describing the molecular skeleton. In benzocyclopropene the hybrids of the carbon atom at the fusion site are $sp^{1.99}$, $sp^{3.20}$, and $sp^{1.34}$, the first two describing the propene ring, the latter being directed outward. In benzocyclobutene the corresponding hybrids show lesser deviations from sp^2 forms. For the C_3 ring the directions of the calculated hybrids deviate from bond directions by the expected values 20–25°, giving the so-called bent bonds. For C_6 rings the deviation angles are close to zero, which gives rise to asymmetrically half-bent bonds where benzene joins the small rings. The calculated hybrids are used for a prediction of spin–spin coupling constants $J_{C^{13}-H}$ which are discussed and compared with the experimentally available data.

The hybridization model has been found very useful for discussion of such molecular properties as bond angles, bond lengths, bond energies, spin–spin coupling constants, proton acidities, etc.[2] Approximate hybridization parameters may be found by transforming available semiempirical molecular orbitals to localized orbitals. An alternative procedure arises from use of localized models, one or which is the method of maximum overlap.[3] This method utilizes the assumption that a large bond overlap results in a stronger bond. Although this approach is based on intuitive concepts and cannot be derived rigorously from the first principles, it is expected to yield useful results in systems with covalent bonding.[4] Moreover an application to a large number of structurally related molecules, like for example hydrocarbons, may be expected to give a good description of many molecular properties.

In this paper we consider an application of the maximum overlap method to two highly strained fused-ring hydrocarbons, benzocyclobutene and benzocyclopropene. This work is a continuation of the study of fused-ring systems initiated by the work on biphenylene and benzo[1,2:4,5]dicyclobutene.[5] These molecules are characterized by unusual constraints and are of considerable interest as their aromatic ring will produce changes in bond lengths, and as a consequence unusual spectral and chemical properties are expected.[6] The simple description in terms of sp^2 and sp^3 hybrids is clearly not adequate for such molecules. More general hybrids of the form sp^n, where n is not restricted to integers 2 and 3, lead to a problem of establishing the hybrid exponent n. The situation is complicated by the presence of opposing tendencies of individual hybrids to increase or decreasd their s content and to reorient as to balance the total bond overlap. The molecular structure of benzocyclobutene and benzocyclopropene introduces bond angles of 150 and 180° which indicate that the hybrids must have unusual s–p content.

The maximum overlap method has been described in the literature.[2-4] Briefly, we search for optimal exponents n of all individual sp^n hybrids of a given molecule which would make a sum of suitably weighted bond overlaps maximum. The weighting factors are introduced to account for the fact that the bond overlap–bond energy ratio is different for CH and CC bonds. These factors take care of a "scaling" of the problem

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[1] (a) Part I: *J. Amer. Chem. Soc.*, **93**, 64 (1971). (b) During the academic year 1972–1973 address correspondence to Department of Chemistry, Harvard University, Cambridge, Mass. 02138.

[2] M. Randić and Z. B. Maksić, *Chem. Rev.*, **72**, 43 (1972).

[3] (a) M. Randić and Z. Maksić, *Theor. Chim. Acta*, **3**, 59 (1965); (b) L. Klasinc, Z. Maksić, and M. Randić, *J. Chem. Soc. A*, 755 (1966).

[4] R. J. Bartlett and Y. Öhrn, *Theor. Chim. Acta*, **21**, 215 (1971).

[5] M. Randić and Z. B. Maksić, *J. Amer. Chem. Soc.*, **93**, 64 (1971), part I in this series.

[6] E. Vogel, W. Grimme, and S. Korte, *Tetrahedron Lett.*, 3652 (1965).

so that it corresponds as close as possible to an energy minimization principle. Recently Bartlett and Öhrn[4] have shown that for predominantly covalent systems the minimum energy and the maximum overlap matrices approximately commute. This implies that it is possible to obtain approximate wave functions solely from a diagonalization of the overlap matrix. The weighting procedure introduced in the maximum overlap method only improves the approximate commutation of the overlap and the energy matrices. Indirectly this is supported by the similarities between the maximum overlap hybrids and those calculated by more ambitious methods.[7] The exponent n of hybrids centered on the same carbon atom are subject to the orthogonality conditions

$$1 + (n_{ij}n_{ik})^{1/2} \cos \theta_{jk} = \begin{matrix} 0 \text{ for } j \neq k \\ 1 \text{ for } j = k \end{matrix} \qquad (1)$$

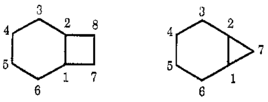
where θ_{ik} is the angle between the directions of hybrids ϕ_{ij} and ϕ_{ik}. The exponent n and the coefficients of s and p orbital in a hybrid are simply related: $n = (b/a)^2$ (a is the coefficient of s, and b of p orbital). The best hybrid parameters are found by a systematic variations of all independent parameters.

Results

Benzocyclobutene.—The molecule is assumed planar,[8] and the standardized bond lengths for hydrocarbons suggested by Dewar and Schmeising[9] have been adopted. The aromatic CC bond is taken to be 1.40 Å. The molecular geometry and numbering of atoms is shown in Chart I. Clementi double ζ-type orbitals are adopted in the calculations.[10] The basic overlap integrals are available for atomic separations of interest.[11]

CHART I

SCHEMATIC DIAGRAMS AND NUMBERING OF ATOMS FOR BENZOCYCLOBUTENE AND BENZOCYCLOPROPENE



Benzocyclobutene has four nonequivalent carbon atoms leading to eight independent hybrids. Once these eight hybrids are selected the s–p composition of the remaining hybrids is determined by the orthogonality relationships in eq 1. We selected the hybrids ϕ_{12}, ϕ_{16}, ϕ_{61}, ϕ_{65}, ϕ_{56}, ϕ_{54}, ϕ_{71}, and ϕ_{78} as the set to be optimized. To reduce the calculations we also assumed the deviation angles, d, at benzene carbons C_5 and C_6 to be equal at each atom separately: $d_{54} = d_{56}$ and $d_{65} = d_{61}$. Since these atoms constitute a strain-free part of the benzene ring, the deviation angles are expected to be close to zero, and the assumption is hardly a restriction. The deviation angles d_{12}, d_{16}, and d_{17} at carbon C_1 may differ considerably and have to be determined separately (subject only to the constraint that all bonds lay in a plane). Since hybrids ϕ_{12} and ϕ_{16} are varied in the optimization procedure a choice of the pair of exponents n_{12} and n_{16} determines all interhybrid angles at C_1 (eq 1). Thus the only remaining parameter is the angle of rotation of the three hybrids relative to the molecular skeleton. When the angle of rotation is found, the deviation angles follow from geometrical considerations. The calculation is then repeated for another set of n_{12} and n_{16}, until the weighted sum of bond overlaps is maximum. The best hybrids, the corresponding bond overlaps and deviation angles are listed in Table I.

TABLE I

CALCULATED MAXIMUM OVERLAP HYBRIDS, BOND OVERLAPS, INTERHYBRID ANGLES, AND ANGLES OF HYBRID DEVIATIONS FROM THE INTERNUCLEAR LINE

Hybrids	Bond overlaps	Interhybrid angles, deg	Deviation angles, deg
	Benzocyclobutene		
$\phi_{12} = \mathrm{sp}^{2.160}$	$S_{12} = 0.7216$	$\theta_1^{26} = 120.6$	$d_{12} = -9.3$
$\phi_{17} = \mathrm{sp}^{2.088}$	$S_{17} = 0.6616$	$\theta_1^{67} = 121.3$	$d_{17} = 16.1$
$\phi_{71} = \mathrm{sp}^{3.326}$		$\theta_7^{18} = 107.6$	$d_{71} = 11.6$
$\phi_{16} = \mathrm{sp}^{1.780}$	$S_{16} = 0.7332$		$d_{16} = 9.9$
$\phi_{61} = \mathrm{sp}^{2.170}$		$\theta_6^{15} = 121.0$	$d_{61} = 0.5$
$\phi_{65} = \mathrm{sp}^{1.784}$	$S_{56} = 0.7309$		$d_{65} = 0.5$
$\phi_{56} = \mathrm{sp}^{1.928}$		$\theta_5^{46} = 121.3$	$d_{56} = 0.7$
$\phi_{78} = \mathrm{sp}^{3.304}$	$S_{78} = 0.6407$		$d_{78} = 8.6$
$\phi_{5H} = \mathrm{sp}^{2.164}$	$S_{5H} = 0.7406$		
$\phi_{6H} = \mathrm{sp}^{2.137}$	$S_{6H} = 0.7412$		
$\phi_{7H} = \mathrm{sp}^{2.728}$	$S_{7H} = 0.7233$		
	Benzocyclopropene		
$\phi_{12} = \mathrm{sp}^{3.203}$	$S_{12} = 0.6662$	$\theta_1^{26} = 118.9$	$d_{12} = -15.8$
$\phi_{16} = \mathrm{sp}^{1.336}$	$S_{16} = 0.7461$	$\theta_1^{67} = 127.8$	$d_{16} = 14.7$
$\phi_{61} = \mathrm{sp}^{1.890}$			$d_{61} = 1.1$
$\phi_{17} = \mathrm{sp}^{1.994}$	$S_{17} = 0.6152$		$d_{17} = 35.0$
$\phi_{71} = \mathrm{sp}^{3.858}$		$\theta_7^{12} = 105.0$	$d_{71} = 25.0$
$\phi_{56} = \mathrm{sp}^{1.928}$	$S_{56} = 0.7417$		$d_{56} = 0.6$
$\phi_{65} = \mathrm{sp}^{1.812}$		$\theta_6^{15} = 122.7$	$d_{65} = 1.1$
$\phi_{54} = \mathrm{sp}^{1.920}$	$S_{45} = 0.7390$	$\theta_5^{46} = 121.3$	$d_{54} = 0.6$
$\phi_{5H} = \mathrm{sp}^{2.164}$	$S_{5H} = 0.7406$		
$\phi_{6H} = \mathrm{sp}^{2.352}$	$S_{6H} = 0.7369$		
$\phi_{7H} = \mathrm{sp}^{2.399}$	$S_{7H} = 0.7295$		

Of particular interest are the hybrids at carbon C_1, which describe the most strained molecular fragment. We obtained $\phi_{12} = \mathrm{sp}^{2.16}$, $\phi_{17} = \mathrm{sp}^{2.09}$, and $\phi_{16} = \mathrm{sp}^{1.78}$ while $\mathrm{sp}^{1.93}$ is a typical form for CC hybrids in the strain-free part of benzene. Thus the hybrids associated with the cyclobutene ring have increased their p content, while the hybrid directed outward consequently increased its s content, in agreement with findings for other four-membered rings.[12] The deviation angles at C_5 and C_6 are practically zero (justifying the assumption that the deviation angles at each atom are equal). The deviation angles at C_1 and C_7 are appreciable, about 10° and more. Hybrids describing the bond C_1–C_6 have a considerably different deviation angle:

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(7) Z. B. Maksić and M. Randić, *J. Amer. Chem. Soc.*, submitted for publication.

(8) G. Fraenkel, Y. Asaki, M. J. Mitchell, and M. P. Cava [*Tetrahedron*, **20**, 1179 (1964)] discuss the possibility of nonplanar cyclobutene ring of benzocyclobutene. From the experimental geminal J_{HH} spin–spin coupling constants using the Karplus equation they deduce for the dihedral angle between adjacent CH bonds of the four-membered ring the value 40°. The puckering, though significant, is not expected to produce dramatic changes in hybrids. The amount of the change can be, for example, estimated by comparing hybrids in some polyacetylenes for which results have been given for planar and puckered conformation: M. Randić and A. Rubčić, *J. Mol. Struct.*, **14**, 193 (1972).

(9) M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **5**, 166 (1959); **11**, 96 (1960).

(10) E. Clementi, *IBM J. Res. Develop.*, **9**, 2 (1965).

(11) L. Klasinc, D. Schulte-Frohlinde, and M. Randić, *Croat. Chem. Acta.*, **39**, 125 (1967).

(12) M. Randić, "Tables of Hybrids Calculated by the Maximum Overlap Method," under preparation. Results for some 30 small-ring hydrocarbons are available on request.

d_{16} close to 10° while d_{61} approaches zero (about 0.5°). Because at one end of the bond there is an appreciable deviation while at the other end the deviation is negligible, the corresponding bond is characteristically asymmetrical and has been referred to as a half-bent bond type.[5]

The bond overlaps found indicate some deviations from the assumed standard bond lengths if bond overlap–bond length correlation is used for theoretical predictions of CC bond lengths.[13,14] The bond overlap S_{78} was found very small, and this points to an increase of the bond length C_7–C_8. This is in agreement with the experimental result in related biphenylene[15] and benzo[1,2:4,5]dicyclobutene.[16] Other bond overlaps show smaller variations in their magnitudes. However, the bond overlap S_{12} is not particularly large, and C_1–C_2 is not predicted as particularly short as the experimental results for biphenylene indicate.[15] It is difficult to explain the discrepancy. The shortening of the C_1–C_2 bond length cannot be due to σ-electron contributions and probably not due to perturbed π electrons either. If future experimental work suggests this to be a typical situation for the bond of fusion when highly strained and relatively strain-free rings are fused, a theoretical explanation will probably require models which go beyond the maximum overlap and the Hückel method.

The perturbation of the σ skeleton of benzene ring will produce changes in the π-electron system, and we can no longer expect the two Kekulé-type valence structures of benzocyclobutene to be equivalent (Chart II). It is difficult, however, to guess which of the two structures is more important. It seems plausible to assume that the four-membered ring which is more strained will dictate the issue. A comparison of the hybrid compositions, bond overlaps, and deviation angles of 1,2-dimethylenecyclobutane and cyclobutene indicates that the exo CC double bonds are relatively strong (bond overlap is 0.7737) while the endocyclic CC double bond is relatively weak (bond overlap is 0.7581).[12] This is because in the former case the tendency of C═C double bonds to increase their s content is supported by the tendency of hybrids involved in small rings to increase their p character, while in the latter case the two contributions are opposing one another. This indicates that structure A will energetically be favored and will have a larger weight. This then agrees with the bond lengths alternation in the strain-free part of the benzene rings of biphenylene (C_1–C_6 = 1.37 Å and C_5–C_6 = 1.42 Å), but is not consistent with the reported unusually short C_1–C_2 bond length.[17] More elaborate SCF–MO calculations, which might clarify the partial inconsistencies between the experimental and theoretical results, are not available. However, the above discussion about the relative weights of the two Kekulé-type structures for benzocyclobutene has some indirect support from calculated Kekulé indices for series of related conjugated polycyclic hydrocarbons.[18] Kekulé indices are defined for individual valence structures and can be calculated from given molecular orbital wave functions. They are defined as projections of selected MO wave functions on various Kekulé structures, and the valence bond structures can be ordered according to the magnitude of this index. The structure with the largest index corresponds to the Kekulé-type structure with the greatest number of formal benzene Kekulé formulas, *i.e.*, to a structure which the empirical Fries rule[19] predicts as the most stable. The Kekulé index is thus indicative of the relative importance of various valence bond structures. Chart III listed Kekulé structures corresponding to the largest value of the Kekulé index for some conjugated systems having the cyclobutadiene ring. In all cases the structures with exocyclic C═C double bonds have been found to have the largest stability. Since we do not expect qualitative change in the relative magnitudes of bond overlaps and the forms of hybrids between benzocyclobutene and benzocyclobutadiene,[20] we may conclude that the information in Chart III indicates rather conclusively that the Kekulé structure A of benzocyclobutene is expected to be more important.

CHART II

KEKULÉ VALENCE BOND STRUCTURES OF BENZOCYCLOBUTENE

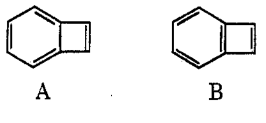
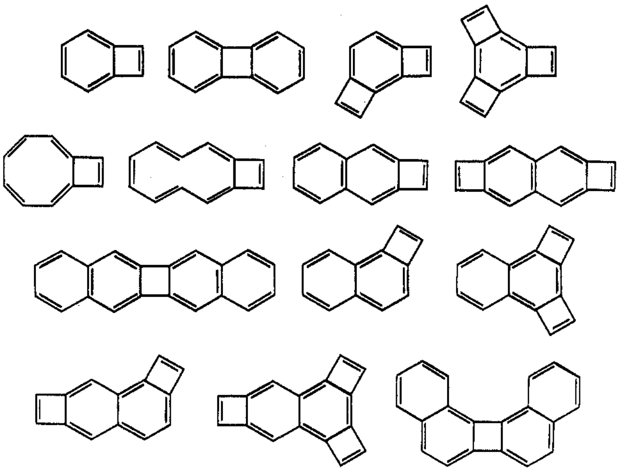


CHART III

VALENCE BOND STRUCTURES WITH THE HIGHEST KEKULÉ INDEX FOR SEVERAL CONJUGATED HYDROCARBONS CONTAINING THE C_4 RING



Benzocyclopropene.—The standard bond lengths were used.[9] The numbering of atoms is shown in Chart I. The maximum overlap hybrids, bond overlaps, and interhybrid and deviation angles are listed in Table I. The hybridization at carbon C_1 is of a par-

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[13] Z. B. Maksić and M. Randić, *J. Amer. Chem. Soc.*, **92**, 424 (1970).

[14] M. Randić, Z. B. Maksić, and M. Eckert-Maksić, *J. Amer. Chem. Soc.*, submitted for publication.

[15] J. K. Fawcett and J. Trotter, *Acta Crystallogr.*, **20**, 87 (1966).

[16] J. L. Lawrence and S. G. G. MacDonald, *Acta Crystallogr., Sect. B*, **25**, 978 (1969).

[17] In three-membered rings CC bonds are even more strained. However the bond lengths are not lengthened and sometimes are even shorter than normal CC single bond. So behavior of CC bonds in C_4 rings are not quite unusual.

[18] A. Graovac, I. Gutman, M. Randić, and N. Trinajstić, submitted for publication.

[19] K. Fries, *Justus Liebigs Ann. Chem.*, **454**, 121 (1927).

[20] Lj. Vujisić, unpublished results, Ph.D. Thesis, University of Zagreb, Zagreb, 1971.

ticular interest because of unusual bond angles for three coplanar bonds: 60, 120, and 180°. To accommodate these angles by three hybrids in a plane is not that simple. As can be seen from Table I, the three hybrids have the following s–p composition: $sp^{1.34}$, $sp^{1.99}$, and $sp^{3.20}$. To indicate the origin of these rather unusual results we will examine the interhybrid angles more closely. If we assume all three hybrids to be sp^2, *i.e.*, interhybrid angles of 120°, we can orient them relatively toward the molecular skeleton so that all deviation angles are 30°. The resulting bending of bonds is too large. It can be reduced by decreasing the angle between ϕ_{12} and ϕ_{17}, while at the same time the interhybrid angle between ϕ_{16} and ϕ_{17} is increased. The interorbital angles between the above hybrids are given by

$$\cos \theta_1^{27} = -(a_{12}/b_{12})(a_{17}/b_{17}) \tag{2}$$

$$\cos \theta_1^{67} = -(a_{16}/b_{16})(a_{17}/b_{17}) \tag{3}$$

A way to meet the above requirements is to decrease the ratio (a_{12}/b_{12}) and increase (a_{16}/b_{16}), while keeping (a_{17}/b_{17}) constant. The orthogonality condition $a_{12}^2 + a_{16}^2 + a_{17}^2 = 1$ still has to be fulfilled. For example, we may consider the following set of nonequivalent trigonal hybrids

$$\phi_{12} = (4/15)^{1/2}\mathrm{s} + (11/15)^{1/2}\mathrm{p} = \mathrm{sp}^{2.75} \tag{4}$$

$$\phi_{16} = (2/5)^{1/2}\mathrm{s} + (3/5)^{1/2}\mathrm{p} = \mathrm{sp}^{1.50} \tag{5}$$

$$\phi_{17} = (1/3)^{1/2}\mathrm{s} + (2/3)^{1/2}\mathrm{p} = \mathrm{sp}^{2} \tag{6}$$

The interhybrid angles are then already changed by about 5° in desirable direction: θ_1^{27} is 115.25° and θ_1^{67} becomes 125.25°. These particular hybrids are better adapted to the special local environment of the carbon atom C_1 than ordinary sp^2 hybrids. If hybrids ϕ_{16} and ϕ_{17} increase their s content and tend to be colinear as much as possible, this would leave ϕ_{12} with very little or no s content, which would result in a very small value of the bond overlap S_{12}. A compromise has to be found. By further reducing the s content in ϕ_{12} and increasing it in ϕ_{16} and allowing ϕ_{17} to vary, we finally arrive at the results given in Table I.

The hybrids describing the benzene ring are not so drastically altered from the idealized sp^2 hybridization types usually assumed for carbons in aromatic molecules. Similarly the hybrids at carbon C_7 have their usual s–p composition characteristic for highly strained three-membered rings. Again, as in biphenylene and benzo[1,2:4,5]dicyclobutene there are half-bent bonds, which it seems are characteristic for molecules having fused rings of which one is highly strained while another is essentially nonstrained.[5]

Correlation with Experimental $J_{C^{13}-H}$ Spin–Spin Coupling Constants

The hybrid s character and the bond overlaps calculated by the maximum overlap method have been found to correlate well with various experimental quantities.[2] In particular $J_{C^{13}-H}$ spin–spin coupling constants, according to the currently accepted views, provide a direct measure of the s character of CH hybrids involved in the formation of C–H bonds. In Table II we compare the experimental and the calculated $J_{C^{13}-H}$ spin–spin constants of benzocyclobutene and benzocyclopropene. For benzocyclobutene the agreement is very good, while in the case of methylene $J_{C^{13}-H}$ of benzocyclopropene the calculated spin–spin constant is too small. The discrepancy, however, is also present in other three-membered rings. For example, in cyclopropane $J_{C^{13}-H}$ is calculated to be 143.0 cps, the experimental value being 161 cps. This difference, about 20 cps, seems to be rather characteristic for calculations on highly strained three-membered rings.[21] The empirical relationship of Muller and Pritchard,[22] $J_{C^{13}-H} = 500a^2$, has been used for deducing the s content of hybrids. If applied on three-membered rings it indicates that hybrids have somewhat higher s content than calculated by the maximum overlap method (and other semiempirical methods). The CH hybrids of three-membered rings should according to an empirical estimate in some cases have s per cent approximately equal to, or even somewhat higher than, the aromatic C–H bonds. In the case of cyclopropane the Muller and Pritchard relationship yields $sp^{2.10}$ methylene hybrids and in benzocyclopropene even $sp^{1.80}$. Characteristic higher infrared frequencies for C–H stretching vibrations of three-membered rings[23] (about 3100 cm^{-1}) indicate, compared with parafinic C–H stretching frequencies (between 2850 to 2950 cm^{-1}), that the empirical estimate is consistent with the data from the vibrational spectroscopy.

TABLE II

A COMPARISON BETWEEN THE EXPERIMENTAL AND CALCULATED $J_{C^{13}-H}$ SPIN–SPIN COUPLING CONSTANTS FOR BENZOCYCLOBUTENE AND BENZOCYCLOPROPENE

	Muller and Pritchard	Modified expression	Experiment
	Benzocyclobutene		
H_6	157.8		158.7 ± 0.8[a]
H_5	159.9		
H_7	133.3	136.9	138.0[b]
	Benzocyclopropene		
H_7	147.1	152.2	178 ± 2[c]

[a] J. W. Emsley, J. Feeny, and L. H. Sutcliffe, "High Resolution N.M.R. Spectroscopy," Vol. 2, Pergamon Press, Oxford, 1966, p 1023; the value shown is for benzene. [b] G. Fraenkel, J. Asaki, M. J. Mitchell, and M. P. Cava, *Tetrahedron*, **20,** 1179 (1964). [c] E. Vogel, W. Grimme, and S. Korte, *Tetrahedron Lett.*, **No. 41,** 3625 (1965).

A more general linear relationship between $J_{C^{13}-H}$ and a^2, which includes the variations of CC bond overlaps,[21] gives somewhat better agreement with the experimental J values than the Muller and Pritchard formula for a number of molecules including benzocyclobutene and benzocyclopropene. In benzocyclobutene the modified J value is within the limits of ±1.0 cps, which is less than a typical experimental error in several reported J values. In benzocyclopropene the J value is increased by 5 cps, which is a significant improvement, though not at all sufficient to eliminate the disagreement between experiment and theory. Calculations on several other three-membered rings indicate that 5 cps is a typical increase for methylene $J_{C^{13}-H}$, while for olefinic CH (in cyclopropene

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(21) Z. B. Maksić, M. Eckert-Maksić, and M. Randić, *Theor. Chim. Acta*, **22**, 70 (1970); Z. B. Maksić, *Int. J. Quantum Chem.*, **5**, 301 (1971); M. Randić, Z. Meić, and A. Rubčić, *Tetrahedron*, **28**, 565 (1972).

(22) N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 768, 1471 (1959).

(23) E. R. Lippincott, *J. Amer. Chem. Soc.*, **73**, 2001 (1951).

rings) the increase is approaching 20 cps.[24] It is evident that the application of more general linear relationship better accounts for the experimental data. But is is not quite clear to what extent the reported improvement is due to the adoption of a linear relationship between J and a^2 (instead of the simple proportionality $J = 500a^2$) or to what extent it arises from inclusion of variations of bond overlaps.

Registry No.—Benzocyclobutene, 4026-23-7; benzocyclopropene, 4646-69-9.

Acknowledgment.—We thank Dr. Jens Oddershede for examining the manuscript and for suggesting several improvements in the presentation.

[24] M. Randić, A. Rubčić, and L. Klasinc, *Tetrahedron*, **27**, 5771 (1971).

Transmission of Substituent Effects in Heterocyclic Systems. The Rates of Solvolysis of Some Substituted 1-(2-Benzofuryl)ethanol Derivatives[1]

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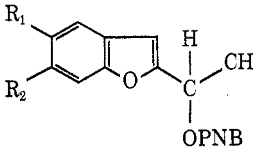
The rates of solvolysis for a series of 5-substituted and 6-substituted 1-(2-benzofuryl)ethanol derivatives (A) have been determined. Though there is excellent correlation of the rates for the 6-substituted compounds with σ_p^+, σ_m^+ fails to give a correspondingly good correlation for the 5-substituted series. Deviations show a clear regularity, with rates for compounds bearing electron donating substituents being too high. A modification of the Dewar–Grisdale equation which uses CNDO/2 molecular orbital parameters to calculate the change in regional charge at the point of attachment of the substituent gives a high quality correlation for both series. These results show that substituents in the 5 position exert their influence more by way of resonance interaction than σ_m^+ would predict.

A number of studies from these laboratories have examined the influence of substituents on reactivity in heterocyclic systems. Information has been presented for furans[3,4] and thiophenes,[5,6] with primary attention being given to solvolysis reactions of the 1-heteroarylethyl derivatives in 80% ethanol. In those studies it was observed that Brown's σ^+ substituent constants[7] were not uniformly successful in predicting relative reactivity in all structural situations. Useful correlations with σ_p^+ were obtained for "conjugating" positions; but σ_m^+ did not generally work well for "nonconjugating" positions.

We have extended these studies to the benzofuran system. A number of substituted 1-(2-benzofuryl)ethanol derivatives (**1**–**9**) have been prepared, and their rates of solvolysis in 80% ethanol have been measured. Table I presents relative rates at 75°. Consideration of these data in two subsets reveals the following. When the 6-substituted series (compounds **1**, **2**, **4**, **6**, **8**; subset A) is considered separately, σ_p^+ gives an excellent correlation (correlation coefficient 0.998) with ρ −3.61. However, the data for the 5-substituted series (compounds **1**, **3**, **5**, **7**, **9**; subset B) show only a fair correlation with σ_m^+. Furthermore, there is a definite trend to the deviations of the 5-substituted series from the least squares line which is defined by the 6-substituted series. Those substituents (methoxy, methyl, and chloro) which effectively donate electrons *via* resonance are clearly above the correlation line. We are therefore led to the conclusion that the 5 position in benzofuran differs from a meta position in benzene in that the sensitivity of the solvolysis reaction toward resonance-donating capability is greater.



A

1, $R_1 = R_2 = H$
2, $R_1 = H$; $R_2 = OCH_3$
3, $R_1 = OCH_3$; $R_2 = H$
4, $R_1 = H$; $R_2 = CH_3$
5, $R_1 = CH_3$; $R_2 = H$
6, $R_1 = H$; $R_2 = Cl$
7, $R_1 = Cl$; $R_2 = H$
8, $R_1 = H_2$; $R_2 = NO_2$
9, $R_1 = NO_2$; $R_2 = H$

TABLE I

RATES OF SOLVOLYSIS OF SUBSTITUTED 1-(2-BENZOFURYL)ETHYL *p*-NITROBENZOATES IN 80% ETHANOL AT 75°

Substituent (compound solvolyzed)	k, sec^{-1}	log k/k_0
H (**1**)	2.45×10^{-5}	0.00
6-OCH_3 (**2**)	7.67×10^{-3} [a]	2.50
5-OCH_3 (**3**)	8.23×10^{-5}	0.53
6-CH_3 (**4**)	2.87×10^{-4}	1.07
5-CH_3 (**5**)	6.80×10^{-5}	0.44
6-Cl (**6**)	6.30×10^{-6}	−0.59
5-Cl (**7**)	1.50×10^{-6}	−1.21
6-NO_2 (**8**)	1.87×10^{-8} [b]	−3.12
5-NO_2 (**9**)	5.12×10^{-8} [b]	−2.68

[a] Extrapolated from rates at lower temperatures. [b] Computed from the rate for the phenylphosphinate, using $k_{pp}/k_{OPNB} = 1.97 \times 10^3$.

The rate data given in Table I have also been fitted to the field and resonance substituent parameters ($\mathfrak{F}$ and

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