

HYBRIDIZATION IN HIGHLY STRAINED SMALL RING HYDROCARBONS*—III

UNSATURATED SPIRO-COMPOUNDS

M. RANDIĆ, A. RUBČIĆ and L. KLASINC
Institute "Rudjer Bošković", Zagreb, Croatia, Yugoslavia

(Received in the UK 15 April 1971; Accepted for publication 25 August 1971)

Abstract—Hybridization in spiro[2.4]hepta-4,6-diene (I), spiro[2.4]hepta-2,4,6-triene (II) and spiro[4.4]nona-2,4,6,8-tetraene (III) is considered by applying the method of maximum overlap. The hybrids of the spiro carbon in I and II differ considerably from the sp^3 -case. The presence of the carbon rings of different size leads to nonequivalent hybrids for the central carbon: $sp^{2.60}$ and $sp^{3.49}$, and $sp^{2.58}$ and $sp^{3.53}$ for I and II, respectively. The calculated exponents n of the sp^n -hybrids for CH bonds are correlated with the τ values (chemical shifts) using a previously observed linear correlation $\tau = 5(n - 1)$. The reasons for some deviations from the above correlation are discussed.

MOLECULES having a spiro-carbon atom allow a study of the mutual interactions of the molecular segments separated by spiro-bonds. Two specific interactions have been mentioned in the literature:

(1) A delocalization of the electrons of the carbon-carbon σ -bond, in particular in highly strained small rings, to a suitable oriented π -system of the other part of the molecule.^{1,2}

(2) A delocalization of the π -electrons of CC double bonds separated by an insulating atom, called generally homoconjugation, and in the particular case when a spiro atom separates two conjugated systems, called spiroconjugation.³

Investigations on a few molecules which could exhibit the above interactions, like spiro[2.4]hepta-4,6-diene, spiro[2.4]hepta-2,4,6-triene, and spiro[4.4]nona-2,4,6,8-tetraene have been interpreted as supporting the presence of the specific σ to π delocalization in the diene, and the π to π delocalization (spiroconjugation) in the triene and the tetraene. However, in these molecules specific structural (geometrical) features are also present which need to be characterized. By examining these molecules by the method of maximum overlap, which is based strictly on a localized model, the part of the changes in molecular geometry and electron distribution which are due to the specific structural environment of the spiro carbon atom may be isolated.

Here we report the hybridization in spiro[2.4]hepta-4,6-diene (I), spiro[2.4]hepta-2,4,6-triene (II), and spiro[4.4]nona-2,4,6,8-tetraene (III), by applying the method of maximum overlap.^{4,5}

However, before discussing the hybrids and overlap integrals we have to comment on possible delocalization in these molecules. The conclusion that some delocalization

* Part I.: *Croat. Chem. Acta* **42**, 425 (1970)
Part II.: *Croat. Chem. Acta* (in press)

exists in these molecules through the specific interactions (1) and (2), mentioned above, is based predominantly on their UV spectra. But the electronic spectra of several unsaturated molecules, including fulvene, trimethylene-cyclopropane, and higher *n*-radialenes, have been interpreted not invoking a delocalization of π -electrons in the ground electronic state, with which we are concerned, but only in the excited states.⁶

The molecules considered possess interesting structural groupings the study of which will further contribute to our knowledge of hybridization in unsaturated hydrocarbons. The *s*-*p* content of the hybrids of the central spiro carbon are of considerable interest. In the first approximation in diene I and triene II they can be described as sp^3 . However the molecular symmetry is C_{2v} , and the pairs of tetrahedral bonds describing rings of different size need not be equivalent in their *s*-*p* content, and in fact are expected to differ. For example in tetracyclopropylidene the spiro carbon joins three and four membered rings and the corresponding hybrids are found to be $sp^{3.31}$ and $sp^{2.73}$, respectively.⁷ Even in tricyclopropylidene with two non-equivalent three membered rings joined by a spiro atom the hybrids differ from sp^3 , although the difference is small in this case.⁷ All this indicates that the maximum overlap method is sufficiently sensitive to distinguish between similar, but not identical, atomic environments.

The method of maximum overlap has been described in detail in earlier work.^{4, 5, 7} We assume therefore that the method and the notation is familiar and will only report the results.

RESULTS

Spiro[2.4]hepta-4,6-diene (I), spiro[2.4]hepta-2,4,6-triene (II) and spiro[4.4]nona-2,4,6,8-tetraene (III), considered in this paper are illustrated in Fig. 1. Compounds II and III have to our knowledge not been synthesized. The various carbon atoms of I-III in Fig. 1, are designated by numbers in such a way that like groupings of atoms retain the same numbering in different molecules, thus facilitating comparisons.

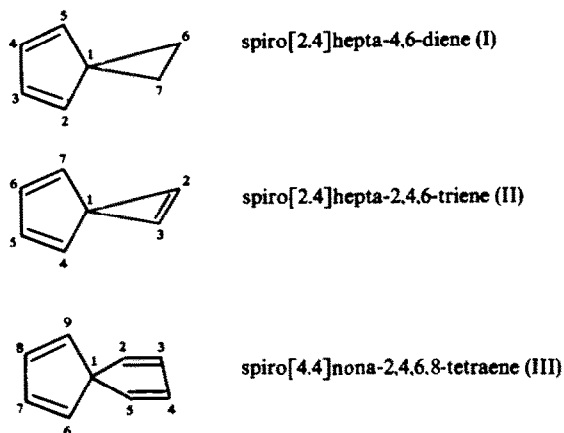


FIG 1. Schematic diagram and numbering of atoms in the investigated unsaturated spiro-compounds

TABLE I. THE MAXIMUM OVERLAP HYBRIDS, THE BOND OVERLAPS AND THE ANGLES OF DEVIATION OF HYBRIDS FROM THE BOND DIRECTIONS, FOR SOME SPIRO-COMPOUNDS

Spiro[2.4]hepta-4,6-diene				Spiro[2.4]hepta-2,4,6-triene			
Hybrid ^a	a	n ^b	S	Hybrid ^a	a	n	S
12	0-5268	2-61	0-67940	12	0-5284	2-52	0-67981
21	0-5461	2-35		21	0-5462	2-35	
23	0-6103	1-69	0-76395	23	0-6103	1-69	0-76395
32	0-6049	1-73		32	0-6049	1-73	
34	0-5539	2-26	0-69985	34	0-5539	2-26	0-69985
16	0-4717	3-49	0-60159	16	0-4699	3-53	0-61842
61	0-4542	3-85		61	0-5159	2-76	
67	0-4554	3-82	0-59831	67	0-5899	1-87	0-72322
2H	0-5739	2-04	0-74326	2H	0-5738	2-04	0-74325
3H	0-5721	2-06	0-74287	3H	0-5721	2-06	0-74287
6H	0-5414	2-41	0-73568	6H	0-6212	1-59	0-75257

Interorbital angles^c:
 $\theta_1^{2,5} = 112^\circ 35'$, $\theta_2^{3,3} = 120^\circ 09'$, $\theta_3^{2,4} = 120^\circ 22'$, $\theta_1^{2,5} = 112^\circ 47'$, $\theta_2^{1,3} = 120^\circ 09'$, $\theta_3^{2,4} = 120^\circ 22'$.
 $\theta_1^{6,7} = 106^\circ 39'$, $\theta_6^{1,7} = 105^\circ 07'$, $\theta_1^{6,7} = 106^\circ 28'$, $\theta_6^{1,7} = 116^\circ 06'$

Deviation angles^d:
 $d_{12} = 6^\circ 17'$, $d_{23} = 5^\circ 16'$, $d_{34} = 5^\circ 23'$, $d_{12} = 6^\circ 24'$, $d_{23} = 5^\circ 17'$, $d_{34} = 5^\circ 23'$.
 $d_{16} = 24^\circ 20'$, $d_{61} = 23^\circ 34'$, $d_{16} = 27^\circ 05'$, $d_{61} = 26^\circ 07'$

Spiro[4.4]nona-2,4,6,8-tetraene							
Hybrid	a	n	S	Hybrid	a	n	S
12	0-5000	3-00	0-67260	34	0-5538	2-26	0-69976
21	0-5465	2-35		2H	0-5747	2-03	0-74344
23	0-6091	1-70	0-76370	3H	0-5720	2-06	0-74285
32	0-6051	1-73					

Interorbital angles:
 $\theta_1^{2,5} = 109^\circ 28'$, $\theta_2^{1,3} = 120^\circ 05'$, $\theta_3^{2,4} = 120^\circ 22'$

Deviation angles:
 $d_{12} = 4^\circ 44'$, $d_{23} = 5^\circ 15'$, $d_{34} = 5^\circ 23'$

^a The first number indicates the atom on which the hybrid is based; the second number, the atom towards which it points.

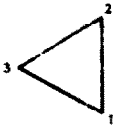
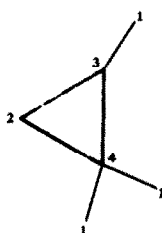
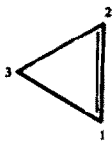
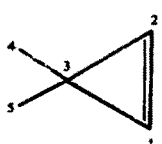
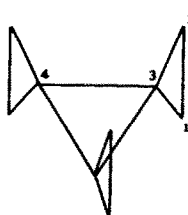
^b In the formulation sp^n .

^c $\theta_i^{j,k}$ is the angle at atom i between the hybrids ij and ik .

^d d_{ij} is the angle between bond ij and the direction of the ij hybrid.

The hybrid orbital ϕ_{ij} is directed from carbon atom i to carbon atom j , and with another orbital ϕ_{ji} contributes to the overlap S_{ij} of a bond C_i-C_j . Hybrids directed towards hydrogens are designated as ϕ_{iH} , ϕ_{jH} . Table I summarizes the results: the hybrids, the bond overlaps, the interorbital angles and the deviation angles. The local environment of the spiro carbon varies in the molecules considered. In the calculation all the degrees of freedom (compatible with symmetry) were allowed to vary, except that deviation angles δ_{ij} of the same carbon are assumed same, i.e. $d_{21} = d_{23}$, $d_{32} = d_{34}$ but $d_{32} \neq d_{23}$. In diene I and triene II the planar cyclopentadiene ring is attached to cyclopropane (saturated) and cyclopropene (unsaturated) rings, respectively. Finally

TABLE II. COMPARISON OF THE CC HYBRIDS IN SPIRO-COMPOUNDS WITH THE AVAILABLE HYBRIDS IN SOME STRUCTURALLY SIMILAR MOLECULES

	Hybrid	a	n
Cyclopropane 	12=21	0.4534	3.86 ^a
1.1.2-Trimethylcyclopropane 	23=24	0.4534	3.86 ^b
	32=34	0.4592	3.74
	42	0.4676	3.57
	31	0.5275	2.59
	41	0.5304	2.55
	14=13	0.4710	3.51
Cyclopropene 	21	0.5913	1.86 ^c
	23	0.5098	2.85
	32	0.4475	3.99
3.3-Dimethylcyclopropene 	12	0.5961	1.81 ^d
	13	0.5126	2.81
	31	0.4607	3.71
	34	0.5365	2.47
Tricyclopropylidene 	12	0.4609	3.71 ^e
	13	0.4572	3.78
	31	0.5010	2.98
	34	0.4990	3.02

^a ref. 5.^b ref. 14.^c ref. 15.^d ref. 16.^e ref. 7.

tetraene III has a symmetrical structure (point group D_{2d}), which requires four equivalent bonds at the spiro carbon, which is thus symmetry forced into sp^3 hybridization.

Firstly, we observe by examining the entries in Table I that the hybrids and the bond overlaps in the cyclopentadiene part of molecules I–III are practically the same, excluding of course the hybrids of the spiro carbon. They are entirely comparable with the maximum overlap calculations on cyclopentadiene,⁸ and indicate that the calculated hybrids are transferable between related molecules, or more correctly, parts of molecules for which the geometrical and structural details are very similar. This is possible because the perturbations on one atom, here spiro carbon, are not transmitted beyond the nearest neighbours. The hybrids in the cyclopropane and cyclopropene parts of the molecules I and II can be compared with the available hybrids in structurally similar molecules (Table II). We see that hybrids in Table II which belong to carbon atoms which are not substituted, show lesser variations. Hybrids at the carbon atom which is substituted in both cyclopropane and cyclopropene containing molecules depend strongly on the nature of the substitution and differ among themselves considerably.

It remains to examine the hybrids at the spiro carbon. In our molecules the spiro carbon joins two rings of different size in molecule I and II. Three membered rings, being considerably more strained, will compete for higher p-content in their hybrids and reduce to some extent the large bending of C—C bonds. The result is an increase from sp^3 to $sp^{3.49}$ and $sp^{3.53}$ for the spiro bonds directed to cyclopropane and cyclopropene rings, respectively. The remaining spiro bonds directed towards the cyclopentadiene ring are enriched in their s character consequently, and become $sp^{2.60}$ and $sp^{2.58}$, respectively, for molecules I and II. These results are intermediate between the cases when hybrids are free to adopt an optimal s–p content, as in cyclopropane, and when they are forced by symmetry to take sp^3 form (*cf.* Table II). The spiro carbon hybrids are consistent with the results on tetracyclopropylidene and tricyclopropylidene. Here instead of a five membered ring we have four membered and three membered rings joined to another three membered ring by a spiro carbon, forming a series: $sp^{3.50}$, $sp^{3.30}$, $sp^{3.00}$ with increase of strain in the other ring.

COMPARISON WITH EXPERIMENTAL DATA

A linear correlation between the exponent n in sp^n and the chemical shift is found for a large number of hydrocarbons.⁹ The correlation lacks an adequate theoretical explanation, but has support in a few empirical relationships. Thus atomic populations for a number of molecules are correlated with proton chemical shifts and give a linear dependence.¹⁰ Similarly Hückel molecular orbital electron densities give a linear fit to the experimental τ -values for several cyclic systems C_nH_n . This indicates that the empirical relationship between chemical shifts τ and the exponents n is not fully unexpected. A plot of the C—H bond overlap against the exponent n is essentially linear in the important region (from $n = 0.75$ to beyond $n = 4.5$) as seen from Fig. 3. in ref. ⁹ Therefore the correlation with n can be converted to correlation with C—H bond overlap. This is closer in its meaning to atomic populations or electron density (or bond orders in π -systems), as it is directly proportional to the electronic charge in the bond. Further support for this is given by the established correlation between bond overlaps and bond lengths for C—H bonds.¹¹

Before using the empirical relationship $\tau = 5(n - 1)$ we should observe that there are systems, in particular molecules having three membered rings and molecules having several CC double bonds, even when separated by more than one atom, which show marked deviations. Other factors influencing the position of the protonic absorption have been discussed¹², and some of them may play an important role in highly strained small rings. Nevertheless, the proton chemical shifts of several molecules having three membered rings show a constant displacement, all falling close to a line represented by: $\tau = 5n - 2$ (Fig. 2 ref. 9). Proton signals in molecules having CC double bonds occur at lower τ -values than predicted by the correlation based predominantly on data from saturated hydrocarbons. Thus in norbornene and norbornadiene the experimental τ values are 4.07 and 3.25, respectively,¹³ while the expected values based on n calculated by the maximum overlap method are approximately 5.0.⁴ All this indicates that we can expect difficulties in correlating the calculated and the experimental chemical shifts in molecules like spiro[2.4]hepta-4,6-diene, when both of these deviations are present. In fact, when we compare the experimental τ -values¹ of 3.23 and 3.56 for olefinic and 8.38 for cyclopropyl hydrogens, with the calculated values of 5.16 for olefinic and 10.06 for cyclopropyl hydrogens, we see the amount of disagreement. The experimental olefinic chemical shifts are not so different from those in norbornadiene, and the same is true for the cyclopropyl chemical shifts which have a typical value found in other molecules containing C₃ rings. It is not quite certain if the origin of these displacements of chemical shifts is due to contributions from partial ring currents, (supporting the suggestion of Clark and Fiato about the aromaticity *via* cyclopropyl conjugation, *i.e.*, σ -bond participation in delocalization of the cyclopentadienyl part of molecule) or due to other factors, or perhaps both. The chemical shifts, as discussed, are not sufficiently reliable to give a definite answer. The calculated hybrid coefficients for CH bonds of compounds I–III can be used for predicting J_{CH} spin–spin coupling constants. Table III gives the values based on the Muller–Pritchard relationship¹⁷ $J(C^{13}-H) = 500a^2$.

TABLE III. PREDICTED $J(C^{13}-H)$ VALUES, CALCULATED BY THE MULLER AND PRITCHARD RELATIONSHIP AND BY THE MODIFIED EXPRESSION WHICH INCLUDES BOND OVERLAP VARIATION FOR THE MOLECULES CONSIDERED

Molecule	Calculated $J(C^{13}-H)$	
	Muller and Pritchard $J_{CH} = 500 a^2$	Modified expression $J_{CH} = 1079a^2/(1 + S^2) - 54.9$
Spiro[2.4]hepta-4,6-diene (I)		
C ₂ —H	164.7	174.0
C ₃ —H	163.6	172.7
C ₆ —H	146.6	150.3
Spiro[2.4]hepta-2,4,6-triene (II)		
C ₂ —H	164.6	173.9
C ₃ —H	163.6	174.2
C ₆ —H	192.9	210.9
Spiro[4.4]nona-2,4,6,8-triene (III)		
C ₂ —H	165.1	174.6
C ₃ —H	163.6	172.6

and also the modified expression¹⁸: $J(C^{13}-H) = 1079a^2/(1 + S^2) - 54.9$, where a is the coefficient of the (2s) orbital of the relevant CH bond hybrid and S is the CH bond overlap calculated by the maximum overlap method.

Most of what has been said could be stated without resorting to maximum overlap hybrids and the accompanied empirical correlations between n and τ . But by using the maximum overlap results we can eliminate the role of the skeletal strain in σ -framework on the considered molecule, which could not be ignored *a priori*. Namely, a plot of HMO π -electron densities *vs.* chemical shifts¹ which is linear and satisfactory for the series of molecules having five, six, seven and eight membered rings, need not necessarily imply that the expected changes in hybridization due to angular distortion in these cyclic structures are minor and can be neglected. These effects may also be linear and therefore only affect the overall linear expression. We expect this to be the case, which future calculations will show. The maximum overlap calculations thus play a complementary role in these investigations, rather than contributing to or detracting from a particular model of delocalization.

Acknowledgement—We thank Mr. G. W. Schnuelle for reading the manuscript and suggesting several improvements in the presentation of the material.

REFERENCES

- ¹ R. A. Clark and R. A. Fiato. *J. Am. Chem. Soc.* **92**, 4736 (1970)
- ² S. W. Staley. *Ibid.* **89**, 1532 (1967)
- ³ A. L. Goodman and R. H. Eastman, *Ibid.* **86**, 908 (1964); M. Y. Lukina, *Russ. Chem. Rev.* 419 (1962)
- ⁴ M. Randić and Z. Maksić. *Theoret. Chim. Acta* **3**, 59 (1965)
- ⁵ L. Klasinc, Z. Maksić and M. Randić, *J. Chem. Soc. (A)*, 755 (1966)
- ⁶ E. Heilbronner. *Theoret. Chim. Acta* **4**, 64 (1966); P. A. Straub, D. E. Meuche and E. Heilbronner. *Helv. Chim. Acta* **49**, 517 (1966); W. T. Simpson. *J. Am. Chem. Soc.* **73**, 5363 (1951)
- ⁷ M. Randić and L. Jakab. *Croat. Chem. Acta* **42**, 425 (1970)
- ⁸ M. Randić, Lj. Vujisić and Z. B. Maksić (to be published).
- ⁹ M. Randić and Z. Majerski. *J. Chem. Soc. (B)*, 1289 (1968)
- ¹⁰ F. J. Weigert and J. D. Roberts. *J. Am. Chem. Soc.* **90**, 3543 (1968)
- ¹¹ Z. B. Maksić and M. Randić, *Ibid.* **92**, 424 (1970)
- ¹² P. G. Maslov, *J. Phys. Chem.* **72**, 1914 (1968); A. Veillard, *Tetrahedron Letters* 2627 (1965)
- ¹³ F. A. Bovey (Ed.), *NMR Data Tables for Organic Compounds*. Vol. 1. Interscience Publishers, New York. (1967)
- ¹⁴ M. Randić, D. Stefanović and L. Klasinc. *Acta Chim. Acad. Sci. Hung.* **50**, 301 (1966)
- ¹⁵ M. Randić and S. Borčić. *J. Chem. Soc. (A)*, 586 (1967)
- ¹⁶ M. Randić, Z. Meić and A. Rubčić, *Tetrahedron* in press
- ¹⁷ N. Müller and D. E. Pritchard. *J. Chem. Phys.* **31**, 768, 1471 (1959)
- ¹⁸ Z. B. Maksić, M. Eckert-Maksić and M. Randić. *Theoret. Chim. Acta* in press