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Geometry of Molecules. Part 4. Iterative Maximum Overlap Calculations of Interatomic Distances, Bond Angles and Strain Energies in Some Rotanes and Related Spiro-Compounds

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The iterative maximum overlap approximation (IMOA) is applied to a series of [n]-rotanes and some related spiro-compounds of unusual topology. The properties of these molecules were discussed in terms of the local hybrid orbitals and extent of their overlapping. Necessity of a clear distinction between bond length and interatomic distance in strained systems is pointed out. Considerable shortening of the C—C interatomic distance of the central carbocycles in [n]-rotanes was established. It was rationalized by the bent bond concept. The delocalization of the pseudo-pi electrons around the central ring in [n]-rotanes is briefly discussed. Angular strain energy and its distribution over the molecular fragments was quantitatively considered in the studied compounds. The strain and heat of formation of spiro (3.3) heptane are favourably compared with available ab initio results.

INTRODUCTION

A large family of cyclic and polycyclic hydrocarbons involving one or more small rings have attracted considerable attention of organic chemists in the last three decades[1]. These compounds take a part in a vast number of chemical reactions due to a pronounced reactivity which is a consequence of high strain inherent in the three and four membered carbocycles. On the other hand, strained molecules exhibit frequently quite unusual features providing thus a serious challenge to contemporary models and theories of chemical bonding. It is not surprising therefore that an immense number of papers appeared in the literature which have dealt with the electronic structure of strained systems. The methods utilized for that purpose had widely different levels of sophistication ranging from simple and qualitative discussions of molecular strain energies to rigorous ab initio calculations[2–10]. The pictorial model of variable hybridization developed in our laboratory proved also useful in rationalizing a large body of local properties of highly strained hydrocarbons[11,12]. The optimal hybridization parameters were evaluated by the maximum overlap approximation (MAO). The method is capable to provide heats of formation and strain energies in a satisfactory manner[11]. An iterative

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version of the maximum overlap approach (IMOA) predicts the interatomic distances and bond angles with a good accuracy[12]. Therefore it seems worthwhile to extend IMOA method to the interesting class of rotanes and some related compounds. These molecules possess at least one spiro-junction carbon atom which joins two molecular fragments embedded in mutually perpendicular planes. Since the exo carbocycles are three or four membered rings these systems have a substantial amount of strain energy. It is interesting to make an approximate estimate of their heats of formation and get some insight into the distribution of angular strain over the molecular skeletons formed by carbon atoms. This investigation is complement to the earlier study on polycyclic organosilicon species[13]. It is desirable also to get some information about the size and shape of these systems. Knowledge of the molecular architecture is the first step in understanding the behaviour of electrons in chemical compounds, and reliable estimates of equilibrium geometries would be advantageous. The accurate ab initio calculations with sufficiently large and flexible basis set require a lot of effort. They are either too expensive or unfeasible as yet for large systems. The IMOA results are therefore of some value particularly because the experimental data are not very abundant.

METHOD

The MOA method is based on an intuitive idea that atoms are building blocks of molecules. The binding energies are only small fractions of the total molecular energy. Consequently, it is plausible to assume that the electronic wavefunctions of atoms are only slightly disturbed in the chemical environments. The influence of the neighbours is reflected in mixing of the nearly degenerate atomic orbitals. The resulting linear combinations, called hybrids, possess appropriate directional properties. They are of the form

$$\psi_{Ai} = a_{Ai}\ (2s) + (1 - a_{Ai}^2)^{1/2}\ (2p)_i \tag{1}$$

if mixing of the atomic wavefunctions with principal quantum number $n=2$ is considered. Here A is the nucleus in question and a_{Ai} denotes a hybridization parameter which can take all positive values between 0 and 1 ($0 \leqslant a_{Ai} \leqslant 1$) It is further supposed that the hybrid orbitals allocated to the same atom are orthogonal. This requirement provides constraints to the free variation of hybridization parameters. Thus the following equations should be satisfied:

$$a_{Ai}\, a_{Aj} + (1 - a_{Ai}^2)^{1/2}\, (1 - a_{Aj}^2)^{1/2} \cos \vartheta_{ij} = 0 \qquad (i, j = 1 \ldots 4) \tag{2}$$

where ϑ_{ij} is the angle between the symmetry axes of the hybrids ψ_{Ai} and ψ_{Aj}. It equals the geometrical angle if there is no bending from the internuclear lines. Equations (2) provide simple means for the calculation of interhybrid angles. It can be easily shown that in small rings the bent bond necessarily appear[4,15,16]. Then the interhybrid angle does not coincide with the geometrical one. Instead, they are related by the formula.

$$\vartheta_{Aij,\,BC} = \vartheta_{BAC} + \delta_{AiB} + \delta_{AjC} \tag{3}$$

where the geometrical angle is denoted by ϑ_{ABC}. The deviation angles of the hybrids ψ_{Ai} and ψ_{Aj} from the internuclear lines AB and AC are given by δ_{AiB} and δ_{AjC}, respectively. Thus the (2p) orbital can be decomposed into parallel and the perpendicular components relative to the straight line passing through the bonded nuclei

$$(2p)_{Ai} = \cos \delta_{AiB}\, (2p)_{\parallel} + \sin \delta_{AiB}\, (2p)_{\perp} \tag{4}$$

and one can distinguish the sigma and pi type of interactions, i. e. overlapping. The hybridization parameters a_{Ai}, where A assumes all carbon atoms and $i = 1 \ldots 4$, are varied until maximum of the sum of bond overlaps is attained:

$$E_t = \sum_{A-B} k_{AB}\, S_{AB} \tag{5}$$

where the summation is extended over all bonds in a molecule. It is tacitly assumed here that one valence bond coupling scheme prevails. Then it is possible to set up a theoretical model for defining bond energies which is based on localized molecular orbitals. It appears that the total SCF energy of a molecular system can be rearranged so that the integrals over localized orbitals correspond to the inner-core electrons, lone pairs, bonding pairs and to the interactions between them[17]. In our approach only the bonding interactions are considered and they are approximated by the overlap integrals (formula (5)). The constants k_{AB} are adjustable empirical parameters which take into account the difference in bond energy for different bonds. The search of the extremum is performed by the simplex algorithm[18]. The expression (5) is actually based on Mulliken's analysis of the resonance energy term $-2\beta/(1+S)$ appearing in the localized molecular orbitals treatment* of diatomic molecules[19]. It appears that the heats of atomization can be calculated with a fair accuracy if the resonance integral is set equal to

$$\beta = -(1/2)\, PSI \tag{6}$$

where P is an empirical parameter, S is the overlap integral between atomic orbitals participating in a bond formation and I is their average ionization energy. Then the quantity

$$E_{AB} = P_{AB}\, S_{AB}\, I_{AB}/(1 + S_{AB}) \tag{7}$$

is a good measure of the A—B bond energy if the bonding is presumably covalent. The parameter P_{AB} is roughly one for most of sigma bonds. If the product $P_{AB}\, I_{AB}$ is written as a new empirical parameter k_{AB} and if the overlap S_{AB} is neglected in denominator in the expression (7) one straightforwardly obtains the equation (5). We shall assume that the k_{AB} weighting factors depend only on the nature of the constituent atoms A and B in order to keep the number of empirical parameters at minimum. The choice of these parameters was thoroughly discussed in a previous paper[11]. We give here their values (in kcal/mol): $K_{C-C} = 121$ and $k_{C-H} = 136$. The basis set employed is formed by Clementi double-zeta atomic wavefunctions[20] for the valence electrons. The inner-shell 1s electrons were treated as highly localized impenetrable cores which contribute very little to chemical bonding and consequently were neglected. The basic idea behind the iterative maximum overlap approximation (IMOA) is the use of the empirical bond length-bond overlap calibration straight lines of the form

$$d\,(C-H) = K_{CH}\, S_{CH} + L_{CH} \tag{8}$$

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* By localized molecular orbital we mean an MO which is spread over two nuclei.

and

$$d\,(\mathrm{C—C}) = K^{\sigma}_{\mathrm{C-C}}\,(b)\; S^{\sigma}_{\mathrm{C-C}}\,(b) + K^{\pi}_{\mathrm{C-C}}\,(b)\; S^{\pi}_{\mathrm{C-C}}(b) + L_{\mathrm{C—C}} \qquad (9)$$

where $K^{\pi}_{\mathrm{C-C}}\,(b)$ and $K^{\sigma}_{\mathrm{C-C}}\,(b)$ refer to the parameters related to sigma and pi type of interaction of a bent bond. If the C—C bond is axially symmetric, the overlap $S^{\mathrm{C-C}}_{\pi}$ (b) is zero and the contribution of the second term in the formula (9) vanishes. The values of the adjustable parameters employed were obtained by the least squares fit method. They are: $K_{\mathrm{CH}} = —0.869$; $L_{\mathrm{CH}} = 1.726$, $K^{\sigma}_{\mathrm{C-C}}(b) = —1.166$; $K^{\pi}_{\mathrm{C-C}}(b) = —2.278$; $L_{\mathrm{C—C}} = 2.298$ (in Å). It should be pointed out that the parameter $K^{\pi}_{\mathrm{C-C}}\,(b) = —3.30$ Å for bent bonds with bending angles higher than 20^0 is much more appropriate. This value was used in three-membered rings. The constants K_{CH}, $K^{\sigma}_{\mathrm{C-C}}\,(b)$ and $K^{\pi}_{\mathrm{C-C}}\,(b)$ are negative consistent with a simple picture that shorter bond corresponds to larger overlap and vice versa. Interestingly enough, parameter $K^{\pi}_{\mathrm{C-C}}\,(b)$ seems to be more important than its sigma counterpart $K^{\sigma}_{\mathrm{C-C}}\,(b)$. This is somewhat puzzling because it is well known that bent bonds are weaker than the »normal« chemical bonds possessing axial symmetry. Therefore an increase in the bond length could be anticipated if considerable hybrids' bending is present. This contradiction is easily resolved if it is recalled that the bent bond is much better represented by the ridge of the maximum charge density in the region of two directly bonded nuclei. This was qualitatively discussed in terms of hybrids orbitals[21,22] and put subsequently in more rigorous form by Bader et al[23]. The value d(C—C) given by the eq. 9 actually corresponds to the internuclear distance which is strictly speaking different from the bond length. The latter measures a segment of the curve passing through the points of the maximum electron charge density. This definition of the bond length has the proper quantum mechanical foundation because it is based on the charge density which is an observable. In fact, the bent bonds were experimentally established in a number of compounds[24,25]. The shortening of the C—C internuclear distance e. g. in cyclopropane is actually a consequence of the extremely long but bent bond. The latter reflects considerable strain which is partly relieved by putting nuclei closer together. The equilibrium distance is a compromise between the nuclear repulsion and strain relief. The relationships (8) and (9) enable the prediction of bond lengths in saturated hydrocarbons. One starts the calculation with some reasonable initial interatomic distances. The standard values of Dewar and Schmeising[26] clasified according to the canonical hybridization states $sp^n—sp^m$ (n, $m = 1, 2, 3$) serve the purpose. After the optimization of the hybridization parameters, a new improved set of interatomic distances is deduced by using correlations (8) and (9). The whole procedure is then repeated until a consistency between input and output bond distances is achieved. Thus the IMOA approach is a sort of constrained maximum overlap method where the interatomic distances are forced to follow empirical relations (8) and (9). This is of crucial importance because all hybrids are thus treated on the same footing. Any use of the arbitrary set of »standard« bond lengths introduces unnecessary bias due to the implicit dependence of the hybrids on the interatomic distances. It should be also pointed out that independent bond angles are also varied in the IMOA procedure yielding thus the optimum values in the sense of the maximum overlap criterion. We have shown in a series of papers that the IMOA technique is a powerful metod for the estimation of the molecular geometries* of hydrocarbons[12]. Since the calculated hybrid orbitals are intimately related to the strain of the molecular system under study we shall define its notion more precisely. Thermodinamically the strain energy is calculated from the deviations of heats of formation from those predicted on the basis of additivity schemes which hold quite accurately for a chosen set of »unstrained« compounds serving as standards. Our results rely heavily on the method of Schleyer et al.[27]. On the other hand, the strain energy can be structurally attributed to torsions due to nonbonded interactions or angle strain arising from the deviation from the »ideal« $109^0 28'$ and 120^0 geometrical angles. It can also result from the bond stretching or bond compression. We shall be concerned in this paper with angular strain only although strictly speaking it is closely related to the bond stretching strain if the bond lenghts are properly defined (vide supra).

RESULTS AND DISCUSSION

The IMOA method was applied to a series of polycyclopropylidenes ([n]-rotanes, where n = 3, 4, 5 and 6) and some related spiro-compounds. It was assumed that the central rings in [n]-rotanes are planar. This is probably not true for [5]- and [6]-rotanes but it considerably reduces the number of variable parameters. Thus the computation for [5] and [6]-rotanes should be considered as model calculations. Some of the studied systems were recently synthetized[28]. The calculated hybridization parameters $n_{Ai} = (1 - a_{Ai}^2)/a_{Ai}^2$, hybrids'deviation angles and overlap integrals are listed in Table I. The main feature of our variable hybridization model are noninteger values of the n_{Ai}^2 parameters. Survey of the results shows that hybrids as a rule deviate from their cannonical states n = 1, 2, 3. However, these deviations are sometimes quite small. An excellent example is provided by the C_1 carbon atom of the central ring in [3]-rotane, where the emanating hybrids from it are roughly of the sp^3 type. This feature deserves some more comment and it will be discussed in more detail. We shall consider in particular the effect of the insertion of spiroannelated cyclopropyl groups on the small rings. The hybrid orbitals describing C—C bonds in cyclopropane and cyclobutane are $sp^{3.69}$—$sp^{3.69}$ and $sp^{3.38}$—$sp^{3.38}$, respectively[12]. Their C—C counterparts in [3] and [4]-rotanes are formed by $sp^{2.96}$—$sp^{2.96}$ and $sp^{2.75}$—$sp^{2.76}$ hybrids exhibiting thus significant increase in s-character accompanied with the concomitant increase in hybrids' deviation angles (roughly ~ 2^0). Both changes cause a decrease (vide infra) in the corresponding C_1—C_1 interatomic distance in [n]-rotanes (n = 3, 4). These findings are not unexpected if the flexibility of the relevant molecular fragments are analysed. The HCH angle of methylene groups in cyclopropane and cyclobutane is an independent geometrical parameter which is optimized in our approach by employing the maximum overlap criterion. Therefore the hybrids ψ (CH) achieve favourable $sp^{2.49}$ and $sp^{2.68}$ compositions for cyclopropane and cyclobutane, respectively, possessing thus relatively high s-characters. Since the total s-character is a constant and the hybrid orbitals are normalized one

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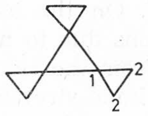
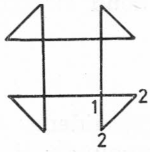
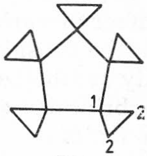
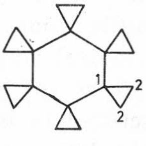
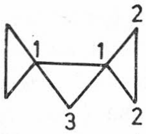
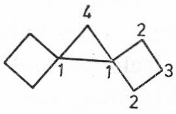
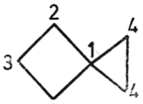
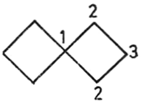
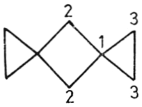
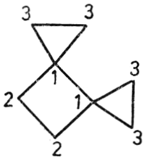
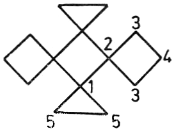
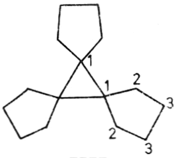
* Bond angles enter the calculation through the relations (2) and (3).

TABLE I

The Calculated Hybridization Ratios, Overlap Integrals and the Deviation Angles of the Hybrid, Orbitals for Some Rotanes and Related Spiro-Compounds as Obtained by the IMOA Method

Molecule	Bond A—B	Hybridizatoin $n_A — n_B$	Overlapping		Deviation Angle deg.
			sigma	pi	
 I	C_1—C_1	2.96—2.96	0.604	0.038	$\delta_{11} = 24.8$
	C_1—C_2	3.03—3.58	0.593	0.035	$\delta_{12} = 24.1$
	C_2—C_2	3.76—3.76	0.574	0.033	$\delta_{21} = 23.2$
	C_2—H	2.49	0.733	—	$\delta_{22} = 23.2$
 II	C_1—C_1	2.76—2.76	0.657	0.007	$\delta_{11} = 10.6$
	C_1—C_2	3.26—3.62	0.587	0.034	$\delta_{12} = 23\ 6$
	C_2—C_2	3.73—3.73	0.575	0.033	$\delta_{21} = 23.1$
	C_2—H	2.49	0.733	—	$\delta_{22} = 23.1$
 III	C_1—C_1	2.58—2.58	0.680	0	$\delta_{11} = 2.4$
	C_1—C_2	3.52—3.66	0.582	0.033	$\delta_{21} = 23.1$
	C_2—C_2	3.70—3.70	0.577	0.033	$\delta_{21} = 22.9$
	C_2—H	2.48	0.733	—	$\delta_{22} = 22.9$
 IV	C_1—C_1	2.47—2.47	0.686	0.001	$\delta_{11} = -3.1$
	C_1—C_2	3.70—3.69	0.578	0.032	$\delta_{12} = 22.8$
	C_2—C_2	3.69—3.69	0.578	0.032	$\delta_{21} = 22.9$
	C_2—H	2.48	0.733	—	$\delta_{22} = 22.9$
 V	C_1—C_1	2.92—2.92	0.607	0.038	$\delta_{11} = 24.6$
	C_1—C_3	3.05—3.64	0.589	0.036	$\delta_{13} = 24.4$
	C_1—C_2	3.01—3.59	0.593	0.035	$\delta_{12} = 24.1$
	C_2—C_2	3.76—3.76	0.574	0.033	$\delta_{22} = 23.1$
	C_2—H	2.50	0.733	—	
	C_3—H	2.51	0.732	—	
 VI	C_1—C_1	3.21—3.21	0.595	0.036	$\delta_{11} = 23.5$
	C_1—C_2	2.80—3.25	0.644	0.005	$\delta_{12} = 9.7$
	C_1—C_4	3.23—3.66	0.586	0.034	$\delta_{21} = 9.2$
	C_2—C_3	3.44—3.41	0.629	0.005	$\delta_{23} = 8.8$
	C_2—H	2.50	0.732	—	$\delta_{32} = 8.4$
	C_3—H	2.67	0.728	—	$\delta_{14} = 23.8$
	C_4—H	2.66	0.728	—	$\delta_{41} = 23.3$

Molecule	Bond A—B	Hybridizatoin $n_A — n_B$	Overlapping		Deviation Angle deg.
			sigma	pi	
 VII	C_1—C_2	2.87—3.40	0.636	0.008	$\delta_{12} = 12.5$
	C_2—C_3	3.38—3.31	0.635	0.003	$\delta_{21} = 10.4$
	C_1—C_4	3.13—3.59	0.590	0.034	$\delta_{23} = 7.2$
	C_4—C_4	3.74—3.74	0.575	0.033	$\delta_{32} = 6.1$
	C_2—H	2.67	0.728	—	$\delta_{14} = 23.9$
	C_3—H	2.73	0.726	—	$\delta_{41} = 23.1$
	C_4—H	2.49	0.733	—	$\delta_{44} = 23.1$
 VIII	C_1—C_2	3.00—3.36	0.639	0.005	$\delta_{12} = 9.2$
	C_2—C_3	3.44—3.41	0.628	0.004	$\delta_{21} = 8.9$
	C_2—H	2.66	0.728	—	$\delta_{23} = 8.7$
	C_3—H	2.65	0.728	—	$\delta_{32} = 8.5$
 IX	C_1—C_2	2.77—3.38	0.643	0.006	$\delta_{12} = 9.7$
	C_1—C_3	3.24—3.63	0.587	0.034	$\delta_{21} = 9.4$
	C_3—C_3	3.72—3.72	0.576	0.033	$\delta_{13} = 23.7$
	C_2—H	2.67	0.728	—	$\delta_{31} = 23.1$
	C_3—H	2.49	0.733	—	$\delta_{33} = 23.0$
 X	C_1—C_1	2.74—2.74	0.659	0.006	$\delta_{11} = 10.4$
	C_1—C_2	2.82—3.36	0.643	0.006	$\delta_{12} = 9.9$
	C_2—C_2	3.41—3.41	0.629	0.005	$\delta_{21} = 9.3$
	C_1—C_3	3.25—3.61	0.588	0.034	$\delta_{22} = 8.7$
	C_3—C_3	3.75—3.75	0.575	0.033	$\delta_{13} = 23.6$
	C_2—H	2.67	0.729	—	$\delta_{31} = 23.1$
	C_3—H	2.50	0.733	—	$\delta_{33} = 23.1$
 XI	C_1—C_2	2.76—3.00	0.652	0.006	$\delta_{12} = 10.1$
	C_2—C_3	3.00—3.39	0.639	0.005	$\delta_{21} = 10.2$
	C_3—C_4	3.42—3.45	0.628	0.005	$\delta_{23} = 9.3$
	C_1—C_5	3.27—3.64	0.587	0.034	$\delta_{32} = 8.6$
	C_5—C_5	3.67—3.67	0.578	0.033	$\delta_{34} = 8.8$
	C_3—H	2.66	0.728	—	$\delta_{43} = 8.5$
	C_4—H	2.63	0.728	—	$\delta_{15} = 23.5$
	C_5—H	2.51	0.733	—	$\delta_{51} = 23.3$
					$\delta_{55} = 23.0$
 XII	C_1—C_1	3.48—3.48	0.585	0.034	$\delta_{11} = 23.3$
	C_1—C_2	2.60—3.13	0.665	0.000	$\delta_{12} = 1.3$
	C_2—C_3	3.22—3.18	0.647	0.000	$\delta_{21} = 1.1$
	C_3—C_3	3.18—3.18	0.649	0.000	$\delta_{23} = 0.2$
	C_2—H	2.83	0.723	—	$\delta_{32} = 0.1$
	C_3—H	2.82	0.723	—	$\delta_{33} = 0.2$

concludes that considerable p-character is transferred to energetically less favourable C—C bonds in these small ring compounds. The situation is quite different in [3]-rotane. The $C_2C_1C_2$ angle of the spiroannelated cyclopropyl ring is quite rigid because its three carbon atoms form an almost perfect equilateral triangle. Thus the nearest neighbours of the spiro-junction carbon form a local field of the slightly distorted tetrahedral symmetry (C_{2v}). The symmetry is not rigorously of the T_d type because C_2 atoms of the methylene groups are not strictly speaking equivalent to C_1 neighbouring atoms. However, their spatial arrangement is very close to the tetrahedral one and all four hybrids are practically of the sp^3 type. It follows that the relatively high s-content of the $\psi(C_1—C_1)$ hybrids in [3]-rotane is a consequence of the high local symmetry of the participating atoms. The symmetry of the C_1 atoms in [4]-rotane is also of the C_{2v} species but in contrast to [3]-rotane the distortion from the T_d symmetry is much more pronounced. The $C_1C_1C_1$ angle is here 90^0 which is at considerable variance with 60^0 of the $C_2C_1C_1$ angle of the spiroannelated cyclopropyl ring. Since the cyclobutane ring is less strained than the cyclopropyl structural unit one can anticipate an increase in the s-character of the former. This is the origin of the significant difference in $\psi(C_1C_1)$ and $\psi(C_1C_2)$ hybrid orbitals which assume values $sp^{2.76}$ and $sp^{3.26}$, respectively. The same conclusion holds for [5] and [6]-rotanes. It is interesting to compare the hybrids of the central ring in [n]-rotanes and cycloalkanes $(CH_2)_n$ where $n = 3 \ldots 6$. The hybridization parameters decrease in the latter from 3.69 to 3.0 as n takes values n = 3, 4, 5, 6 while in the former series it falls from roughly 3.0 to as low as 2.47 in [6]-rotane. The $C_1—C_2$ bonds of the peripheral cyclopropyl units in [3]-rotane has higher average s-character than in the corresponding cycloalkane $(CH_2)_3$. However, the average s-character decreases along the series of higher rotanes reaching cyclopropane value for $n = 5$.

An interesting question arises whether the cyclopropyl rings which are in [n]-rotanes linked to one another in s-cis fashion could lead to an electron system delocalised over the central ring. Fitjer and Conia concluded on the basis of spectroscopic evidence that such an delocalization in [3]-rotane is to be excluded[28(f)]. They also suggested that the delocalization of the pseudo-pi orbitals formed by the bent hybrid orbitals $\psi(C—C)$ of the perpendicular C—C bonds is the more probable the smaller the angle β between the planes of the two neighbouring cyclopropane rings and the greater the p-content of the $\psi(C—C)$ exo-hybrids. In order to examine this idea in more quantitative terms we shall use the results presented in Table I. For this purpose we shall consider a particular C—C bond of the central carbocycle. The local coordinate systems are oriented as shown in Figure 2. Simple algebra yields the following formula for the calculation of an overlap integral between the hybrids ψ_i and ψ_2:

$$\begin{aligned}\langle \psi_1 | \psi_2 \rangle = {} & [1/(1+n)] \langle 2s_1 | 2s_2 \rangle + [n/(1+n)] [-\cos^2\varphi \cos(\vartheta_{CCC}/2) \langle 2p_{x1} | 2p_{x2} \rangle_\sigma + \\ & + \sin^2\varphi \cos^2(\vartheta_{CCC}/2) \langle 2p_{y1} | 2p_{y2} \rangle_\pi + \sin^2(\vartheta_{CCC}/2) \langle 2p_{z1} | 2p_{z2} \rangle^\pi] + \\ & + [2\sqrt{n}/(1+n)] [-\cos\varphi \cos(\vartheta_{CCC}/2) \langle 2s_1 | 2p_{x2} \rangle] \qquad (10)\end{aligned}$$

where n is the hybridization parameter $n = (1 - a^2)/a^2$ of the hybrids ψ_1 and ψ_2, which in turn are equivalent. The planes involving hybrids ψ_1 and ψ_2

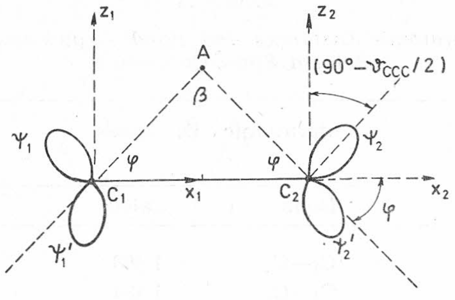


Figure 1. Schematic representation of the molecules studied in this paper.

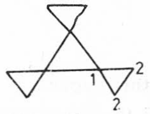
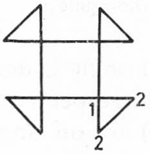
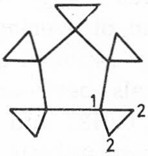
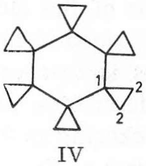
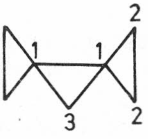
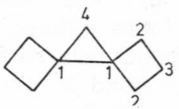
Figure 2. Overlapping of the ψ (C—C) hybrids describing exo-bent bonds of the central ring in [n]-rotanes. The angle between the two planes involving the hybrid orbitals in question is denoted by β. These planes bisect the angles of the regular central poligon at the respective sites C_1 and C_2. They are inclined to the central C_1—C_2 bond by the angle φ.

are perpendicular to the regular central polygon. Their mutual angle is denoted by β. These planes bisect the angles of the central ring at the respective sites C_1 and C_2. They are inclined to the C_1—C_2 bond (Figure 2) by an angle ψ. The angles β and φ are related by an obvious formula $\varphi = 90^0 - \beta/2$. Thus, in [3]-rotane for example the value of φ and β are 30^0 and 120^0, respectively. The subscripts σ and π in the formula (10) refer to sigma and pi overlapping of atomic orbitals. The numerical analysis supports the aforementioned qualitative conclusion of Fitjer and Conia. The overlap integrals between the neghbouring C—C exo-hybrids of the central ring are 0.016, 0.0121 and 0.175 for [n]-rotanes where n takes the values n = 3, 4, 5 and 6 respectively. One observes a steady increase in overlapping along the series which has quite substantial values in [5]- and [6]-rotanes. Complete treatment of the electron delocalization around the central carbocycle is easily performed following the approach of Julg and Julg[29]. However, detailed analysis is reserved for a later paper. It is interesting to notice that the hybrids describing central carbocycle are bent inside ($\delta_{11} = -3.1^0$). Consequently, its puckering may lead also to some relief of angular strain of the central ring. The rest of the results given in Table I speak for themselves.

The interatomic distances and the relevant bond angles are presented in Table II. The salient feature of the results for [n]-radialenes is a shortening of the internuclear distances of the central carbocycle relative to that in the corresponding cycloalkane. This is, as discussed earlier, a consequence of the extremely long bond panths in highly strained rings. They may be diminished only at the expense of the increased internuclear repulsion because the nuclei are put close together. The equilibrium distances are results of a compromise between these two opposite effects. The spiro-bonded cyclopropyl rings exihibit the same shortening of the C_1—C_2 bonds in [3]- and [4]-rotanes although in considerably smaller extent. On the contrary, the C_2—C_2 bonds are slightly longer than that in cyclopropane. In [5]- and [6]-rotanes the bond lengths in cyclopropyl units are practically equal to the cyclopropane value. The results for other compounds fit the same picture. For example, the spiro C—C bond in VIII is shorter than in cyclobutane while the peripheral C_2—C_3 bond is

TABLE II

The Predicted Interatomic Distances and Bond Angles in Some Rotanes and Related Spiro-Compounds

Molecule	Interatomic Distances Å		Bond Angles/deg	
	Bond	Calcd	Angle	Calcd
 I	C_1—C_1	1.468	$C_2C_1C_2$	61.2
	C_1—C_2	1.494	$C_1C_2C_2$	59.4
	C_2—C_2	1.520	HC_2H	113.6
	C_2—H	1.089		
 II	C_1—C_1	1.516	$C_2C_1C_2$	60.8
	C_1—C_2	1.503	$C_1C_2C_2$	59.5
	C_2—C_2	1.519	HC_2H	113.7
	C_2—H	1.089		
 III	C_1—C_1	1.504	$C_2C_1C_2$	60.3
	C_1—C_2	1.512	$C_1C_2C_2$	59.9
	C_2—C_2	1.518	HC_2H	113.7
	C_2—H	1.089		
 IV	C_1—C_1	1.497	$C_2C_1C_2$	60.0
	C_1—C_2	1.518	$C_1C_2C_2$	60.0
	C_2—C_2	1.518	HC_2H	113.7
	C_2—H	1.089		
 V	C_1—C_1	1.467	$C_1C_3C_1$	58.8
	C_1—C_3	1.494	$C_1C_1C_3$	60.6
	C_1—C_2	1.493	$C_2C_1C_2$	61.2
	C_2—C_2	1.520	$C_1C_2C_2$	59.4
	C_2—H	1.089	HC_2H	113.6
	C_3—H	1.089	HC_3H	113.7
 VI	C_1—C_1	1.488	$C_1C_1C_4$	60.3
	C_1—C_2	1.535	$C_1C_4C_1$	59.3
	C_1—C_4	1.502	$C_2C_1C_2$	91.6
	C_2—C_3	1.554	$C_1C_2C_3$	89.1
	C_2—H	1.089	$C_2C_3C_2$	90.2
	C_3—H	1.094	HC_2H	112.0
	C_4—H	1.093	HC_3H	112.1
			HC_4H	113.5

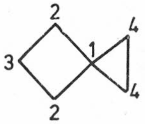
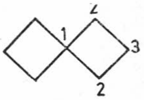
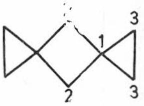
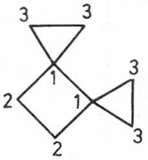
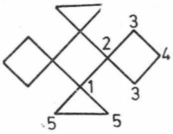
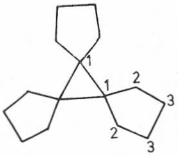
Molecule	Interatomic Distances Å		Bond Angles/deg	
	Bond	Calcd	Angle	Calcd
 VII	C_1—C_2	1.539	$C_2C_1C_2$	85.4
	C_2—C_3	1.551	$C_1C_2C_3$	89.5
	C_1—C_4	1.498	$C_2C_3C_2$	95.5
	C_4—C_4	1.519	$C_4C_1C_4$	60.9
	C_2—H	1.093	$C_1C_4C_4$	59.6
	C_3—H	1.095	HC_2H	112.0
	C_4—H	1.089	HC_3H	111.5
			HC_4H	113.6
 VIII	C_1—C_2	1.541	$C_2C_1C_2$	91.0
	C_2—C_3	1.555	$C_1C_2C_3$	89.5
	C_2—H	1.093	$C_2C_3C_2$	90.0
	C_3—H	1.093	HC_2H	112.1
			HC_3H	112.1
 IX	C_1—C_2	1.535	$C_2C_1C_2$	91.7
	C_1—C_3	1.503	$C_1C_2C_1$	88.3
	C_3—C_3	1.518	$C_3C_1C_3$	60.6
	C_2—H	1.093	$C_1C_3C_3$	59.7
	C_3—H	1.089	HC_2H	111.9
			HC_3H	113.6
 X	C_1—C_1	1.514	$C_2C_1C_1$	90.8
	C_1—C_2	1.536	$C_1C_2C_2$	89.2
	C_2—C_2	1.554	$C_3C_1C_3$	60.7
	C_1—C_3	1.502	$C_1C_3C_3$	59.6
	C_3—C_3	1.520	HC_2H	111.9
	C_2—H	1.094	HC_3H	113.7
	C_3—H	1.089		
 XI	C_1—C_2	1.523	$C_1C_1C_1$	89.0
	C_2—C_3	1.542	$C_2C_1C_2$	91.0
	C_3—C_4	1.555	$C_3C_2C_3$	90.8
	C_1—C_5	1.503	$C_2C_3C_4$	89.7
	C_5—C_5	1.518	$C_5C_1C_5$	60.8
	C_3—H	1.093	$C_1C_5C_5$	59.6
	C_4—H	1.093	HC_3H	112.6
	C_5—H	1.089	HC_4H	112.3
			HC_5H	113.5
 XII	C_1—C_1	1.505	$C_2C_1C_2$	109.9
	C_1—C_2	1.523	$C_1C_2C_3$	107.1
	C_2—C_3	1.543	$C_2C_3C_3$	108.0
	C_3—C_3	1.541	HC_2H	110.6
	C_2—H	1.097	HC_3H	110.7
	C_3—H	1.097		

TABLE III

The Predicted Heats of Formation and Strain Energies for Some Rotanes and Spiro — Compounds

Molecule	Decomposition of Strain Energy		E_s (total)	ΔH_f^0
	Central Ring	Peripheral Rings	kcal/mol	kcal/mol
[3]Rotane	three-membered = 27.1	3 × three-membered = 3 × 25.7	104.3	96.3
[4]Rotane	four-membered = 33.3	4 × three-membered = 4 × 25.5	135.3	105.5
[5]Rotane	five-membered = 3.7	5 × three-membered = 5 × 25.3	129.9	117.6
[6]Rotane	six-membered = 5.3	6 × three-membered = 6 × 25.1		
Trispiro (4.0.4.0.4.0) pentadecane	three-membered = 25.6	3 × five-membered = 3 × 4.4	38.7	—15.1
Spirohexane	four-membered = 27.8	three-membered = 25.6	53.4	32.3
Dispiro (2.0.2.1) heptane	three-membered = 26.4	2 × three-membered = 2 × 25.7	77.9	69.3
Spiro (3.3) heptane	four-membered = 26.2	four-membered = 26.2	52.4	20.2
Dispiro (2.1.2.1.) octane	four-membered = 28.8	2 × three-membered = 2 × 25.5	79.8	60.5
Dispiro (3.0.3.1) nonane	three-membered = 26.1	2 × four-membered = 2 × 26.7	79.5	48.3
Tetraspiro (2.0.3.0.2.0.3.0) tetradecane	four-membered = 31.3	2 × four-membered = 2 × 25.8 2 × three-membered = 2 × 25.5	134.1	95.2

virtually equal to the latter. It is interesting to compare our values with recent ab initio results of Radom et al.[30] for this molecule. They used a modest STO-3G basis set, which usually gives only moderate agreement with experiment. The ab initio bond distances are (in Å): d (C_1—C_2) = 1.549, d (C_2—C_3) = 1.550 d (C_2—H) = 1.087 and d (C_3—H) = 1.087. One observes that ab initio STO-3G method does not discriminate enough between spiro and peripheral C—C bonds and that C—H bond lengths are slightly to low. The results can be favourably compared with the IMOA ones (Table II) otherwise.

The strain energies and heats of formation of the studied system are cited in Table III. Since the IMOA method is based on the local hybrid orbitals it can conveniently provide information about the distribution of strain of molecular systems over their fragments. The strain energies are broken down to the sums of contributions of constituent small rings. The strain energy of the peripheral cyclopropyl units is fairly constant being ~ 25.5 kcal/mol. This value is ~5 kcal/mol lower than the calculated estimate for cyclopropane itself[11]. It is interesting to observe that the four-membered carbocycle is destabilized by the spiro-annelated cyclopropyl rings. In [4]-rotane the central ring possess the strain as large as 33 kcal/mol which should be compared with the IMOA value of 24.6 kcal/mol for cyclobutane[11]. Surprisingly enough the central five-membered ring in [5]-rotane is sligthly stabilized upon insertion of the five cyclopropyl spiro-units. Our estimate of the strain energy in compound VIII of 52.4 kcal/mol can be favourably compared with ab initio value of 56.8 kcal/mol[27]. The same applies for the heats of formation 26.9 kcal/mol and 20.2 kcal/mol, the ab initio result being higher. Other physical properties could be otained by using available correlations[11,12,28] and the results displayed in Table I.

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SAŽETAK

Geometrija molekula. Dio 4. Računanje međuatomskih udaljenosti, kutova između veza i energija napetosti nekih rotana i srodnih spiro-spojeva pomoću iterativne metode maksimalnog prekrivanja

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Iterativna metoda maksimalnog prekrivanja primijenjena je na niz [n]-rotana kao i na neke srodne molekule. Svojstva ovih spojeva diskutirana su pomoću izračunanih hibridnih orbitala. Ustanovljeno je znatno skraćenje međuatomske C—C udaljenosti kod središnjih prstena u rotanima.

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