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Geometry of Molecules. Part 7. Interatomic Distances, Bond Angles and Strain Energies in some Rotenes and Related Spirocompounds by the IMO Method

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The electronic and molecular structure of some three-, four-, five- and six-membered ring rotenes are studied by the iterative maximum overlap method. The shape and size of these unusual, highly strained, systems are considered and the strain destabilization energies are estimated. The local bond characteristics are discussed in terms of variable hybridisation indices. Studied properties include spin-spin coupling constants, C—H stretching frequencies, thermodynamic proton acidities, diamagnetic susceptibilities and the diamagnetic contribution to the nuclear magnetic shielding.

INTRODUCTION

There has been considerable increase of interest in the theory of hybridisation and its application to chemical problems in recent years[1–10]. This trend is not surprising because it is well established by now that hybrid orbitals posses high chemical content. They have proved a useful in discussing a number of local bond features as well as some gross molecular properties which are additive in nature. The variable hybridization model of covalent bonding developed by us is capable of rationalizing a large body of properties of organic and organosilicon compounds such as: spin-spin coupling across one bond[11,12], proton thermodynamic acidity[13], C—H stretching frequencies[14], intrinsic bond energies[15], C—H proton isotropic hyperfine constants in planar radicals[16] and interatomic bond distances and bond angles[8,10,17,18]. The overlap integrals between the directly bonded hybrid orbitals were successfully correlated with heats of formation, heats of hydrogenation and angular strain energies[19,20]. Further, knowledge of structural parameters predicted by the iterative maximum overlap (IMO) method[17,18] allows quite reliable estimates of diamagnetic contributions to molecular magnetic susceptibilities[21] and magnetic shielding of nuclei[22]. It is, therefore, of some interest to apply the IMO method to families of compounds which exhibit unusual properties. In this paper we consider highly strained rotenes and some related spirocompounds depicted in Figure 1. This is an outgrowth of the earlier work on rotanes[7].

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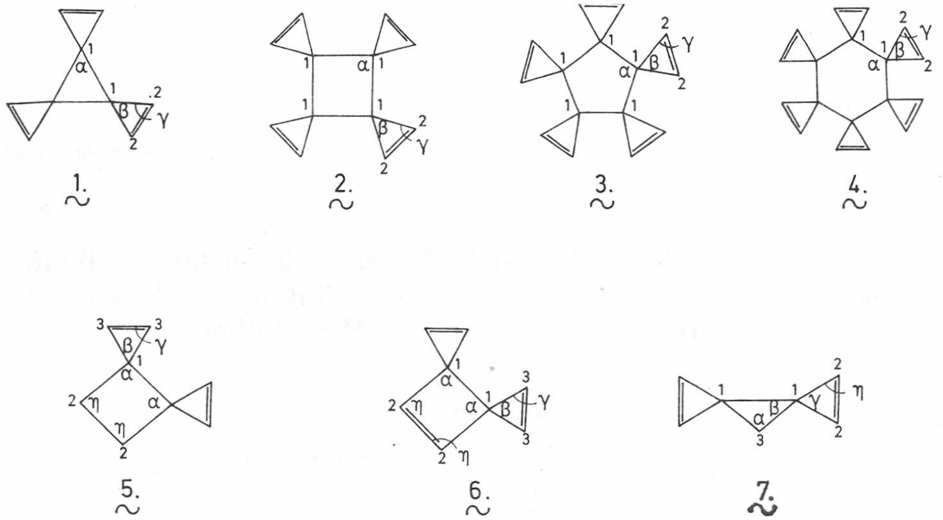

Figure 1.

THE METHOD

The IMO method is thoroughly discussed elsewhere[17,18]. Briefly, it is based on an intuitive idea that atoms retain their identity within a molecule. The influence of the chemical neighbourhood is reflected in mixing of atomic states. The lack of spherical symmetry and anisotropy of the electronic charge distribution around an atom are described by hybrid orbitals.

$$\psi_A = a_A (ns) + (1 - a_A^2)^{1/2} (np_A) \tag{1}$$

where only s and p — type AOs are considered.

Thus the adopted philosophy corresponds to the distorted atom approach. The hybridization parameters a_A in (1) are determined by employing the energy weighted maximum overlap criterion

$$E = \sum_{AB} k_{AB} S_{AB} \tag{2}$$

where the sum encompasses all bonds in a molecule.

It should be mentioned that the number of adjustable weighting factors k_{AB} was kept at a minimum. For example, for hydrocarbons only two parameters (k_{CH} and k_{CC}) are used. In order to avoid unnecessary bias introduced by the »standard« bond distances, an iterative version was designed. The resulting overlap integrals are forced to follow the empirical linear relations with bond interatomic distances[17,18]. Hence, the IMO procedure is the constrained energy weigthed maximum overlap method. The interested reader can find relevant details in previous papers[17,18].

RESULTS AND DISCUSSION

Hybridization

The resulting hybridization sp^n ratios and the deviation angles of the hybrids from the straight lines passing through the bonded nuclei are given in Table I. A salient feature of the results is that in highly strained fragments one observes considerable deviation of the hybridization parameters from the canonical values indicating a necessity to employ the variable hybridization approach where n varies continously in the interval $0 \leq n \leq \infty$. Hence it is more flexible to conform to local environments of the lower symmetry than

TABLE I

The Calculated Hybridization Ratios, σ and π Overlap Integrals and Deviation Angles of the Hybrid Orbitals for some Rotenes and Related Spiro-compounds as Calculated by the IMO Method.*

Molecule	Bond A—B	Interatomic Distances	Hybridization Parameters	Overlapping		Deviation Angles	Geometries Angles
				σ	π		
1	C_1—C_1	1.468	2.97—2.97	0.604	0.038	$\delta_{11} = 24.9$	$\alpha = 60.0$
	C_1—C_2	1.445	3.04—2.58	0.603	0.046	$\delta_{12} = 27.8$	$\beta = 53.7$
	C_2—C_2	1.305	1.91—1.91	0.678	0.049	$\delta_{22} = 27.1$	$\gamma = 63.1$
	C_2—H	1.066	1.65	0.759	0	$\delta_{21} = 26.5$	$HC_2C_1 = 145.5$
2	C_1—C_1	1.517	2.77—2.77	0.657	0.007	$\delta_{11} = 10.6$	$\alpha = 90.0$
	C_1—C_2	1.455	3.26—2.61	0.598	0.045	$\delta_{12} = 27.3$	$\beta = 53.3$
	C_2—C_2	1.304	1.90—1.90	0.679	0.048	$\delta_{22} = 27.0$	$\gamma = 63.4$
	C_2—H	1.066	1.65	0.760	0	$\delta_{21} = 26.4$	$HC_2C_1 = 145.2$
3	C_1—C_1	1.505	2.59—2.59	0.679	0.0	$\delta_{11} = 2.4$	$\alpha = 108.0$
	C_1—C_2	1.465	3.51—2.63	0.592	0.044	$\delta_{12} = 26.8$	$\beta = 52.9$
	C_2—C_2	1.304	1.89—1.89	0.681	0.048	$\delta_{22} = 26.9$	$\gamma = 63.5$
	C_2—H	1.065	1.64	0.760	0	$\delta_{21} = 26.2$	$H_2C_2C_1 = 144.9$
4	C_1—C_1	1.491	2.39—2.39	0.691	0.0	$\delta_{11} = -2.6$	$\alpha = 120.0$
	C_1—C_2	1.510	3.88—2.82	0.574	0.041	$\delta_{12} = 26.9$	$\beta = 51.1$
	C_2—C_2	1.302	1.81—1.81	0.690	0.045	$\delta_{22} = 26.2$	$\gamma = 64.5$
	C_2—H	1.065	1.62	0.736	0	$\delta_{21} = 25.7$	$H_2C_2C_1 = 143.6$
5	C_1—C_1	1.514	2.73—2.73	0.659	0.006	$\delta_{11} = 10.4$	$\alpha = 90.8$
	C_1—C_2	1.536	2.83—3.35	0.642	0.005	$\delta_{12} = 9.9$	$\beta = 53.3$
	C_1—C_3	1.454	3.25—2.61	0.598	0.045	$\delta_{13} = 27.3$	$\gamma = 63.4$
	C_3—C_3	1.304	1.90—1.90	0.679	0.049	$\delta_{33} = 27.0$	$\eta = 89.2$
	C_2—C_2	1.556	3.45—3.45	0.627	0.005	$\delta_{22} = 8.7$	$HC_2C_2 = 118.0$
	C_2—H	1.094	2.67	0.728	0	$\delta_{21} = 9.1$	$HC_2H = 112.0$
	C_3—H	1.066	1.65	0.760	0		$HC_3C_1 = 144.1$
6	C_1—C_1	1.522	2.85—2.85	0.648	0.009	$\delta_{11} = 12.4$	$\alpha = 86.6$
	C_1—C_2	1.505	2.76—2.44	0.664	0.008	$\delta_{12} = 11.9$	$\beta = 53.3$
	C_2—C_2	1.345	1.80—1.80	0.738	0.012	$\delta_{22} = 13.3$	$\gamma = 63.3$
	C_1—C_3	1.453	3.22—2.60	0.599	0.045	$\delta_{13} = 27.4$	$\eta = 93.4$
	C_3—C_3	1.304	1.90—1.90	0.679	0.049	$\delta_{33} = 27.0$	$HC_2C_1 = 129.9$
	C_2—H	1.071	1.84	0.760	0	$\delta_{21} = 11.8$	$HC_3C_1 = 145.3$
	C_3—H	1.066	1.65	0.657	0	$\delta_{31} = 26.4$	$\alpha = 58.8$
7	C_1—C_1	1.466	2.91—2.91	0.608	0.037	$\delta_{11} = 24.5$	
	C_1—C_3	1.495	3.06—3.65	0.589	0.036	$\delta_{13} = 24.5$	$\beta = 60.6$
	C_1—C_2	1.444	3.02—2.58	0.603	0.046	$\delta_{12} = 27.8$	$\gamma = 53.7$
	C_2—H	1.066	1.652	0.759	0	$\delta_{31} = 23.6$	$\eta = 63.1$
	C_2—C_2	1.305	1.91—1.91	0.678	0.049	$\delta_{22} = 27.1$	$HC_2C_1 = 145.5$
	C_3—H	1.090	2.511	0.732	0	$\delta_{21} = 26.5$	$HC_3H = 113.5$
							$HC_3C_1 = 131.8$

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* Distances in Å and angles in degrees.

the sp^3, sp^2 and sp^1 values characteristic of ideal T_d, D_{3h} and C_v arrangements of equivalent neighbouring atoms. It is well known that favourable overlapping of the coupled hybrid orbitals is achieved if several simple rules are obeyed. In the first place, one expects substantial hybridization if s and p orbitals placed on the same nucleus have comparable overlaps with bonded neighbouring atoms[23]. Further, the deviation angles of the coupled pair of hybrid orbitals strive to achieve similar, if not equal, deviation angles as well as hybridization ratios[8,10]. Finally, each bond tries to get as much s-content as possible since the overlap integrals are proportional to s-characters over a large range. It is clear that the resulting hybridization parameters are obtained by an interplay of all these effects taking into account the weighting factors which bring overlaps in line with bond energies. An important feature of strained systems is that axial symmetry of the covalent bonds is lost due to the hybrids bending. An attempt to describe C—C bonds in cyclopropane by complex hybrid orbitals[24] which make an angle of 60^0 failed, because it was subsequently shown that complex hybrids have poor overlapping[25]. Thus the bent bonds necessarily appear in small rings which were discussed first by Förster[26] and elaborated later by Coulson and Moffit[27]. It is interesting to observe that bent bonds were predicted by theory much earlier than they were really observed by X-ray diffraction experiments[28-30]. Bending of hybrids has some important chemical consequences which will be discussed later. We shall mention here that hybrids describing CC bonds in small rings tend to increase their p-character in order to diminish deviation angles, or in other words the angular strain. For instance, the IMO method yields $sp^{3,7}$ hybridization in the cyclopropane ring, while C—H bonds assume energetically favourable $sp^{2,5}$ hybrids[17] leading to relaxation and opening of the HCH angle. In contrast, the cyclopropenyl rings in *1* are rigid and the C—C exo-bonds emanating from the spiro-junction carbon C_1 cannot relax. Therefore the hybridization at C_1 is practically of the sp^3-type. There is a slight redistribution of p-character from the central C_1—C_1 to the exo C_1—C_2 bond since the $\psi(C_1C_2)$ hybrids are then more appropriate to approach the relatively small angle β of 53.7^0. Hence, the spiro-annelation of three cyclopropenyl rings leads to a substantial increase of s-character relative to the cyclopropane value, a feature which is already observed in rotanes[7]. It is interesting to notice rehybridization in the cyclopropenyl carbocycle. The $\psi(C_1C_2)$ hybrid of the $sp^{3.04}$-type has a higher s-content than its counterpart in cyclopropene $(sp^{3.68})$[10]. The rest of the cyclopropenyl fragment is relatively little affected by spiro-annelation. The $\psi(C_2C_1)$ in *1* also has increased s-character $(sp^{2.58})$ relative to the parent compound hybridization $(sp^{2.65})$, compatible with the rule of the maximum possible similarity between the hybrids forming a bond. It is noteworthy to observe also the similarity of deviation angles in C_1—C_2 bonds which take values 27.8^0 and 26.5^0 for δ_{12} and δ_{21}, respectively. Finally, the p-character is slightly increased in the strained double bond in *1* $(sp^{1.91})$ as compared with cyclopropene $(sp^{1.88})$. One has to point out in this connection that we employ the $\sigma - \pi$ separation throughout this work. Considerable increase in s-orbital content is found in central rings of other rotenes. The central bonds in *2* are described by $sp^{2.77} - sp^{2.77}$ hybrids while free cyclobutane has $sp^{3.41}$ hybridization with a pronounced p-character. Analogously, the hybridization ratios of the intra C—C bond in *3* and the corresponding bond in cyclopentane are

2.59 and 3.28, respectively[18]. The largest s-content in the central carbocycles is found in *4* and is as high as 2.39. It appears that the p-character of endo C—C bonds decreases almost uniformly by 0.2 from 3.0—2.4 in the series *1—4*, concomitant with the increase in C—C—C angle of the central ring. The p-character of the $\psi(C_1C_2)$ hybrids increases along the same series from 3.04—3.88 at the expense of the central carbocycles. This is also compatible with a decrease in the apical angles β of the cyclopropenyl fragments. It is interesting to notice the parallel increase in p-character of the $\psi(C_2C_1)$ hybrids which try to follow their $\psi(C_1C_2)$ counterparts. This effect is of the second order. The difference in $\psi(C_1C_2)$ and $\psi(C_2C_1)$ is inevitable because they emanate from four- and three-coordinated carbons, respectively. The approximate equality of deviation angles δ_{12} and δ_{21} is worth mentioning. The bending of hybrid orbitals inside the central ring ($\delta_{11} = -2.6^0$) in *4* indicates that its puckering might be favourable. The high s-character of C—H bonds in *1—4* is comparable to that found in the parent cyclopropene. The hybridization ratios in *5—7* fit the overall picture established by present results and earlier calculations. The bending angles $\delta_{12} \cong \delta_{21}$ and $\delta_{13} \cong \delta_{31}$ are equal to a good approximation. The hybrids describing C_2C_2 bonds in *5* and *6* are very close to those found in parent unsubstituted compounds cyclobutane and cyclobutene, respectively, thus illustrating the transferability of the hybridization parameters characterising bonds which are not directly connected with the substitution sites. The hybrids $\psi(C_1C_2)$ and $\psi(C_2C_1)$ in *5* tend to become similar. The latter has lower p-content than the $\psi(C_2C_2)$ hybrid. In contrast the $\psi(C_1C_2)$ has increased p-character ($sp^{2.83}$) as compared to the $\psi(C_1C_1)$ composition in *2* ($sp^{2.77}$). The same conclusion holds for $\psi(C_1C_3)$ hybrid in 7. These findings support previous conjecture that hybrid orbitals forming a bond strive to have similar size, shape and bending angles.

Structural Properties

As proposed and discussed earlier by us[7,8,10,18,31], it is useful to distinguish between the interatomic bond distance (IBD) and bond length in highly strained systems. The bond length (BL) is defined as a segment of a curve passing through the points of maximum electron density in the region between the linked atoms. Consequently BL and IBD coincide in an axially symmetric covalent bond, but are quite different in a bond deformed by strain. This distinction helps to resolve the bond length paradox appearing in small rings. Let us consider cyclopropane which is an archetype of a strained compound. Its interatomic distance of 1.510 Å is significantly shorter than that found for the C—C distance in unstrained ethane (1.534 Å). This is in sharp contradiction to the lower stability of C—C bonds in cyclopropane which is caused by angular strain. The point is that the bond length defined above is really longer in the cyclopropyl ring. Indeed, if the length of a bent bond is approximated by a segment of a parabola which approaches the bonded nuclei in such a way that the corresponding hybrids are its tangents[31], one obtains in cyclopropane a value of 1.552 Å which is considerably higher than ethane bond length of 1.534 Å. Therefore a strained bond is longer than the strain-free one as measured by the bond lengths, if the constituent atoms have the same coordination numbers. It should be mentioned that the definition of a bond as a ridge of the maximum electron density distribution was suggested independently by Mårtensson and Sperber[32] and later by Bader et al.[33]. It is of some interest to observe that the difference between the BL and IBD is substantial in small rings. Let us consider C_1—C_1 values in the series of compounds *1*, *2* and *3*. The corresponding calculated estimates (in Å) are 1.468 (1.519); 1.517 (1.526) and 1.505 (1.506), respectively, where the interatomic bond distances are given without parentheses. It appears that the difference between BL and IBB is practically non-existent in *3* rotene. An analogous set of values related to C_1—C_2 bonds along the same series is (in Å): 1.445 (1.506); 1.455 (1.526) and 1.465 (1.524), the BL being longer by roughly ~0.06 Å. The IMOM calculations predict appreciable compression of the central C—C interatomic bond distances in rotenes relative to parent molecules, a feature which was already noticed in rotanes. This is a consequence of the dramatic increase in s-characters (vide supra) of hybrids describing C_1—C_1 bonds and the slight increase in their bending. Namely, the hybrids exhibiting large deviations have relatively poor overlapping which can be increased only by a decrese in IBD, i. e. at the expense of the larger internuclear repulsion. Hence, the resulting interatomic distances are a compromise between the favourable overlapping and repulsive core interactions. The estimated IBDs should be taken with due caution because the transannular repulsions and delocalization effects of π- and pseudo-π orbitals are not taken into account. There is some X-ray evidence that central bonds in *1* and *2* rotanes are considerably shortened[34]. However, no noticeable changes were found for *3* and *4* rotanes. Whether this is a consequence of folding of central rings, and/or influence of the interactions mentioned above and omitted in the calculations, remains to be better investigated. In any case, more experimental work on the synthesis of these interesting compounds and their geometric features would be desirable.

Energetic Properties

Assuming the validity of the bond additivity scheme one can easily estimate heats of formation of hydrocarbons by using available correlations with bond overlap integrals[19]. The calculated IMOM ΔH_f values are as a rule in good agreement with experimental results. Discrepancies are usually easily interpreted as special effects like e. g. π-electron delocalization in 1,3-butadiene[19] etc. Therefore, a comparison of computed and experimental data yields useful insight into the electronic structure of the studied systems, interactions

TABLE II

Heats of Formation and Strain Energies in some Rotenes as calculated by the IMO Method (in kJ/mol)

Compound	ΔH_f	E_s
1	1050.8	816.1
2	1358.9	1066.5
3	1570.8	1151.5
4	1904.5	1334.2
5	684.5	584.9
6	1281.9	1310.1
7	721.9	579.2

between separate fragments etc. The predicted ΔH_f values and strain energies E_s for the considered compounds are summarized in Table II. It should be pointed out that strain energy does not have an absolute meaning. It depends on the chosen set of »unstrained« compounds serving as standard, on the assumed ΔH_f additivity scheme or on a set of homodesmotic »gedanken« reactions[35]. Nevertheless, strain energies within the adopted scale give a useful index of relative stabilities. In the systems presently studied the angular strain prevails. We have shown that in these cases strain energy is caused by hybrid bending in small rings[20]. Employing correlations with σ- and π-overlapping of bent bonds calibrated against the strain energy scheme of Schleyer et al.[36], one obtains reasonable estimates of destabilization arising due to angular deformations. It is noteworthy that hybrid orbitals and their bending offer a simple explanation of the distribution of strain over the molecular fragments and its additivity in polycyclic compounds. The strain in the latter is given roughly as a sum of strain energies of the constituent carbocycles[37]. For example, the strain of the rotene *1* of 816 kJ/mole is given to a good approximation as the sum of strain energies of three cyclopropene values[10] (668 kJ) and the cyclopropane estimate[19,20] (130 kJ). The difference between the 816 kJ/mole and the corresponding additive value of 798 kJ/mole illustrates the changes in hybrid composition upon the spiro-annelation of cyclopropyl and cyclopropenyl rings. It is, however, important to stress that a rough idea of the total strain can be obtained by a mere summation of the strain energies of substituent fragments. This is a remarkable feature because strain destabilization energy is not an easily calculated entity, being out of reach of rigorous methods for sizable molecules. Reversing the argument mentioned above, one can decompose the overal strain energy into components related to characteristic structural grouping.

Diamagnetic Properties

The diamagnetic shielding of the ^{13}C carbon nuclei can be easily computed by using the Flygare-Goodisman formula[38]

$$\sigma_{av}{}^{d} = (e^2/3mc^2)\,\langle 0\,|\,1/r\,|\,0\rangle \cong \sigma_{av}{}^{d}\,(\mathrm{FA}) + (e^2/3mc^2)\sum_{\mathrm{A}}{}' Z_{\mathrm{A}}/r_{\mathrm{A}} \qquad (3)$$

once the geometry is known. Here, $\sigma_{av}{}^{d}$ (FA) refers to the free atom value, which for carbon is 260.7 ppm according to the ab initio result of Malli and Froese[39], and summation excludes the nucleus in question placed in the origin of the coordinate system. Other constants have their usual meaning. The Flygare-Goodisman formula (3) tacitly assumes that there is no intramolecular charge transfer, which is a good approximation for hydrocarbons. It should be mentioned that expression (3) works very well even for heteroatomic molecules[40]. This is a consequence of the fact that the electrostatic potential at the nucleus can be quite accurately calculated by the point-charge approximation[41]. It is also expected that the calculated diamagnetic shieldings are not very sensitive to the estimated structural parameters because the interatomic distances appear in the denominator of the operator. The predicted $\sigma_{av}{}^{d}$ (C) shieldings by the IMO method for a number of characteristic hydrocarbons can be favourably compared with the ab initio results[22,42]. The IMOM $\sigma_{av}{}^{d}$ (C) values for rotenes and related spiromolecules studied in this paper are presented in Table III. The great adventage of the point-charge formula (3)

TABLE III

Diamagnetic Shielding of Carbon Atoms as Predicted by the IMO Method (in ppm)

Molecule	Atom	σ_{av}^{d}
1	C_1	287.9
	C_2	282.5
2	C_1	294.5
	C_2	287.5
3	C_1	300.3
	C_2	292.7
5	C_1	287.0
	C_2	282.9
	C_3	282.1
6	C_1	286.4
	C_2	282.4
	C_3	280.0
7	C_1	283.8
	C_2	279.6
	C_3	280.4

is its simplicity and transparency. One can easily estimate the influence of the nearest neighbours on the diamagnetic shielding, the contribution of remote groups etc. The relative values of σ_{av}^{d} (C) shieldings are of some interest. It is evident that tetracoordinated central ring carbon atoms are most shielded because they are surrounded by four carbons which are populated by 6 electrons. The difference between endo and exo carbon shieldings ranges between 3 to 8 ppm, which makes the diamagnetic contribution to chemical shifts.

The diamagnetic susceptibility may be expressed also in a simple form by using the point-charge model[43]

$$\chi_{aa}^{d} = (Ne^2/4\,mc^2)\,[\sum_{A} Z_A\, b_A^2 + \sum_{A} Z_A\, c_A^2 + 2\,n_C + 0.4\,n_H] \qquad (4)$$

where a, b and c are inertial coordinate axes while n_C and n_H are the number of carbon and hydrogen atoms in a molecule, respectively. Other physical constants have their usual meaning. The remaining diagonal elements of the χ^{d}-tensor are obtained by cyclic permutations of coordinates. Formula (4) is a theoretical extension of the empirical rule found for the out-of-plane second moments $\langle c^2 \rangle$ by Flygare et al.[44]. It is based on the atom-in-a-molecule picture, at the same time disregarding charge migration as unimportant. The atoms were consired as spheres possessing zero effective charge. The performance of formula (4) is very good and can be additionally improved by inclusion of the intramolecular charge transfer[46]. In any case, expression (4) holds to a good approximation in hydrocarbons[43] and the results offered by the IMO method are in good accordance with ab initio and experimental data[21,42]. The present results are given in Table IV. It should be mentioned that their accuracy heavily relies on the precision of the estimated coordinates measured from the center of mass of a molecule, because the second moment operators are proportional to their squares. The diagonal elements of the diamagnetic susceptibility and the related second moments give some information about the shape and size of the electron charge cloud in a molecule.

TABLE IV

Second Moments and Diagonal Elements of the Diamagnetic Susceptibility Tensor as Estimated by the IMO Method (in 10^{-16} cm^2 and 10^{-6} cm^3 mol^{-1}, respectively)

Molecule	Second moments	Diamagnetic susceptibilities
1	$\langle a^2\rangle = 120.4$	$\chi_{aa}{}^{d} = -659.3$
	$\langle b^2\rangle = 120.4$	$\chi_{bb}{}^{d} = -659.3$
	$\langle c^2\rangle = 35.0$	$\chi_{cc}{}^{d} = -1021.6$
2	$\langle a^2\rangle = 195.8$	$\chi_{aa}{}^{d} = -1060.6$
	$\langle b^2\rangle = 195.8$	$\chi_{bb}{}^{d} = -1060.6$
	$\langle c^2\rangle = 54.2$	$\chi_{cc}{}^{d} = -1661.3$
3	$\langle a^2\rangle = 291.1$	$\chi_{aa}{}^{d} = -1522.2$
	$\langle b^2\rangle = 291.1$	$\chi_{bb}{}^{d} = -1522.2$
	$\langle c^2\rangle = 67.7$	$\chi_{cc}{}^{d} = -2469.9$
5	$\langle a^2\rangle = 112.9$	$\chi_{aa}{}^{d} = -482.8$
	$\langle b^2\rangle = 80.9$	$\chi_{bb}{}^{d} = -619.8$
	$\langle c^2\rangle = 33.2$	$\chi_{cc}{}^{d} = -820.9$
6	$\langle a^2\rangle = 112.8$	$\chi_{aa}{}^{d} = -433.1$
	$\langle b^2\rangle = 72.6$	$\chi_{bb}{}^{d} = -603.7$
	$\langle c^2\rangle = 29.5$	$\chi_{cc}{}^{d} = -786.5$
7	$\langle a^2\rangle = 49.2$	$\chi_{aa}{}^{d} = -288.9$
	$\langle b^2\rangle = 37.9$	$\chi_{bb}{}^{d} = -336.8$
	$\langle c^2\rangle = 30.2$	$\chi_{cc}{}^{d} = -369.5$

Spin-spin Coupling Constants and Proton Chemical Shifts

The spin-spin coupling constants across one bond are predominantly determined by the local orbital hybridization. One of the present authors suggested the following formula[11]

$$J_{AB} = k_{AB}\,[(s^0/_0)_A\,(s^0/_0)_B/(1 + S_{AB}{}^2)] + l_{AB} \tag{5}$$

where S_{AB} is the overlap integral of the coupled hybrids possessing s-characters $(s^0/_0)_A$ and $(s^0/_0)_B$, respectively, and k_{AB}, l_{AB} are adjustable empirical parameters. Relations of type (5) proved very useful in discussing coupling constants wherever the Fermi contact term is by far the most important contribution. This condition is satisfied for C—H and C—C single bonds[11,47-50]. It is well documented by now that the spin-dipole and orbital-dipole contributions are not negligible for C=C and C≡C bonds[50]. Keeping this in mind we shall use the formula (5) in order to predict the J (CC) and J (CH) coupling constants in the studied series of compounds. It should be mentioned in this connection that the relation (5) is a slight generalization of the earlier Muller-Pritchard formula for C—H bonds[51] and the Frei-Bernstein correlation for directly bonded carbon nuclei[52,53] It is specifically adapted for IMO results which as a rule yield noninteger hybridization states. The predicted coupling constants are given in Table V. One should point out that absolute values are less accurate than the relative changes across the series of related compounds because a large portion of errors tend to cancel out in the latter case. We shall, therefore, discuss the J (C—H) and J (C—C) constants with respect to those found in parent molecules. The estimated J (C—C) constant in cyclopropane[11] is 10 Hz higher than the measured one[54]. Since a similar departure from the true value can be anticipated for the central bond in *1*, an increase of 27 Hz is predicted for the $J\,(C_1—C_1)$ coupling constant which is a consequence of the increase in s-character (Table I). The $J\,(C{=}C)$ constant e. g. in ethylene is also overestimated by 10 Hz. If the calculated value $J\,(C_2{=}C_2)$ in *1* is empirically adjusted for this imperfection one arrives at $J\,(C_2{=}C_2) = 61$ Hz which can be favourably compared with the value of 63 Hz predicted by Figeys et al.[49] and obtained by using the charge dependent atomic orbital exponents and INDO localised molecular orbitals. The latter were produced by the maximum bond charge technique developed by Von Niessen[55]. The J (C—H) coupling in *1* is underestimated by 20 Hz as judged by experiment and Figeys et al.[49] calculations. Nevertheless, the IMO method reflects the increase in the coupling constant of the C—H bond attached to a strained double bond. The J (C—C) constant in cyclobutane (28.2 Hz) is close to the INDO—LMO result of 25.6 Hz[49]. Hence, an increase of the $J\,(C_1—C_1)$ coupling in *2* of roughly ~13 Hz is predicted by present computations. The trend of increasing J (CC) constants in the series *1*—*4* is apparently due to the richer s-content of the corresponding hybrids. It is interesting to mention that there are approximate linear relations between the J (C—H) and J (C—C) coupling constants and the respective ν (C—H) and ν (C—C) stretching frequencies[14,57], which underline the importance of reliable estimates of spin-spin coupling across one bond. To conclude this section one has to stress that there is little doubt about the importance of hybridization in determining coupling constants in hydrocarbons[11,47–54,58], despite some criticism in the literature[59].

The proton chemical shifts were estimated by the simple empirical formula $\tau_H = 5\,(n - 1)$ based on the idea that hybrids richer in p-content screen the neighbouring proton more effectively[60]. The τ_H values presented in Table V clearly show the difference between the coordination numbers of the directly bonded carbon atoms.

GENERAL REMARKS

Distribution of s-character in covalent bonds has important chemical consequences[1,2,61,62]. We have shown that the simple weighted maximum overlap method yields hybridization parameters which can be successfully correlated with a large number of physical and chemical properties of molecules[6–22,42]. It should be mentioned that the Förster-Coulson-Moffitt bent bond picture[26,27] of strained systems is essentially equivalent to the Walsh model[63,64]. The latter was found to be very useful in interpreting PES spectra of polycyclic hydrocarbons within the method developed by Gleiter and Spanget-Larsen[65–67]. The hybrid orbital basis sets are very convenient for the approximate MO schemes because they intrinsically involve necessary polarization and directional properties. The LCHO (linear combination of hybrid orbitals) SCF—CI scheme designed by Meyer and Pasternak was successfully employed to elucidate spectral properties of cyclic and acyclic alkanes[70,71]. The flexibility of hybrid orbitals in describing highly anisotropic atomic environments by using pro-

TABLE V

The Calculated J (CH) and J (CC) Coupling Constants and Proton Chemical Shifts as Obtained by the IMO Method

Compound	Bond	Coupling Const.	Atom	Chemical Shifts
1	C_1—C_1	37.9	H	3.3
	C_1—C_2	41.7		
	C_2—C_2	70.8		
	C_2—H	202.9		
2	C_1—C_1	41.8	H	3.2
	C_1—C_2	47.0		
	C_2—C_2	71.4		
	C_2—H	203.3		
3	C_1—C_1	46.1	H	3.2
	C_1—C_2	44.3		
	C_2—C_2	72.0		
	C_2—H	203.6		
4	C_1—C_1	51.9	H	3.1
	C_1—C_2	31.8		
	C_2—C_2	75.9		
	C_2—H	206.1		
5	C_1—C_1	42.7	(C_2)H	8.3
	C_1—C_2	35.1	(C_3)H	3.2
	C_2—C_2	28.9		
	C_1—C_3	47.1		
	C_2—H	137.3		
6	C_1—C_1	40.2	(C_2)H	4.2
	C_1—C_2	46.4	(C_3)H	3.3
	C_1—C_3	29.7		
	C_2—C_2	75.0		
	C_2—H	187.4		
7	C_1—C_1	39.2	(C_2)H	3.3
	C_1—C_2	41.3	(C_3)H	7.6
	C_2—C_2	70.9		
	C_1—C_3	30.9		
	C_3—H	134.1		

moted AOs and different zetas for different directions has been thoroughly discussed by Del Re[72] and Kirkwood and Cook[73]. Hybrid orbitals also provide a basis for the maximum bond order method devised by Jug[74] while Whitehead and Zeiss[75] found that the constrained MOMO (molecular orbital maximum overlap) method is capable of reproducing the total molecular energy and a number of one-electron properties in a satisfactory manuer*. It follows that Pauling's[1] fruitful idea about the mixing of AOs placed on the same atomic center is a goldmine not yet fully explored.

REFERENCES

1. L. Pauling, *Proc. Nat. Acad. Sci. USA* **72** (1975) 3799, 4200; *ibid.*, **73** (1976) 274, 1403, 4290; *ibid.*, **74** (1977) 2614, 5235; *ibid.*, **75** (1978) 12, 569; *Acta Cryst.* **B35** (1979) 1535; *J. Solid State Chem.* **40** (1981) 266.
2. Z. S. Herman, *Int. J. Quant. Chem.* **23** (1983) 921 and the references cited therein.
3. D. M. Chipman, W. E. Palke, and B. Kirtman, *J. Amer. Chem. Soc.* **102** (1980) 3377.
4. J. P. Foster and F. Weinhold, *J. Amer. Chem. Soc.* **102** (1980) 7211; A. B. Rives and F. Weinhold, *Int. J. Quant. Chem.* **14** (1980) 201.
5. K. H. Aufderheide, *J. Chem. Phys.* **76.** (1982) 1897.
6. M. Eckert-Maksić, K. Kovačević, and Z. B. Maksić, *J. Organomet. Chem.* **168** (1979) 295.
7. K. Kovačević, Z. B. Maksić, and A. Moguš, *Croat. Chem. Acta* **52** (1979) 249.
8. Z. B. Maksić, K. Kovačević, and A. Moguš, *Theoret. Chim. Acta* **55** (1980) 127; *J. Mol. Structure Theochem* **85** (1981) 9.
9. Z. B. Maksić, K. Kovačević, and M. Vampola, *Z. Naturforsch.* **36a** (1981) 1196.
10. M. Eckert-Maksić and Z. B. Maksić, *J. Mol. Structure Theochem* **86** (1982) 325.
11. Z. B. Maksić, *Int. J. Quant. Chem.* **S 5** (1971) 301; Z. B. Maksić, M. Eckert-Maksić, and M. Randić, *Theoret. Chim. Acta* **22** (1971) 70.
12. K. Kovačević and Z. B. Maksić, *J. Mol. Structure* **17** (1973) 203; K. Kovačević, K. Krmpotić, and Z. B. Maksić, *Inorg. Chem.* **16** (1977) 1421.
13. Z. B. Maksić and M. Eckert-Maksić, *Tetrahedron* **25** (1969) 5113.
14. Z. B. Maksić, Z. Meić, and M. Randić, *J. Mol. Structure* **12** (1972) 482; Z. B. Maksić, Z. Meić, and K. Kovačević, *Z. Naturforsch.* **A 28** (1973) 797.
15. Lj. Vujisić and Z. B. Maksić, *J. Mol. Structure* **7** (1971) 431.
16. Z. B. Maksić and K. Kovačević, *Chem. Phys. Letters* **73** (1980) 592.
17. K. Kovačević and Z. B. Maksić, *J. Org. Chem.* **39** (1974) 539; Z. B. Maksić and A. Rubčić, *J. Amer. Chem. Soc.* **99** (1977) 4233.
18. Z. B. Maksić and M. Eckert-Maksić, *J. Mol. Structure Theochem* **91** (1983) 295.
19. K. Kovačević, M. Eckert-Maksić, and Z. B. Maksić, *J. Mol. Structure* **21** (1974) 335; *Croat. Chem. Acta* **46** (1974) 249.
20. Z. B. Maksić, K. Kovačević, and M. Eckert-Maksić, *Tetrahedron Lett.* (1975) 101.
21. Z. B. Maksić and M. Eckert-Maksić, (in preparation).
22. Z. B. Maksić and M. Eckert-Maksić, (in preparation).
23. A. Maccoll, *Trans, Faraday Soc.* **46** (1950) 369.
24. O. Mårtensson and Y. Öhrn, *Theoret. Chim. Acta* **9** (1967) 133.
25. Z. B. Maksić and Lj. Vujsić, *Theoret. Chim. Acta* **14** (1969) 396.
26. Th. Förster, *Z. Phys. Chem.* **B 43** (1939) 58.
27. C. A. Coulson and W. E. Moffitt, *Phil. Mag.* **40** (1949) 1.
28. A. Hartman and F. L. Hirshfeld, *Acta Cryst.* **20** (1966) 80.
29. C. J. Fritchie, Jr., *Acta Cryst.* **20** (1966) 27.
30. P. Coppens, *Angew. Chem.* **89** (1977) 33; P. Coppens and E. D. Stevens, *Adv. Quant. Chem.* **10** (1977) 1 and references cited therein.
31. Z. B. Maksić and M. Eckert-Maksić, *Croat. Chem. Acta* **42** (1970) 433.
32. O. Mårtensson and G. Sperber, *Acta Chem. Scand.* **24** (1970) 1749.

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* see also the ref. (76).

33. G. R. Runtz, R. F. W. Bader, and R. R. Messer, *Can J. Chem.* **55** (1977) 3040.
34. T. Prangé, C. Pascard, A. de Meijere, U. Behrens, J. P. Barnier, and J. M. Conia, *Nouv. Jour. Chim.* **4** (1980) 321.
35. P. George, M. Trachtman, C. W. Bock, and A. M. Brett, *Tetrahedron* **32** (1976) 317.
36. P. R. von Schleyer, J. E. Williams, and K. R. Blanchard, *J. Amer. Chem. Soc.* **92** (1970) 2377.
37. L. N. Ferguson, *J. Chem. Ed.* **47** (1970) 46.
38. W. H. Flygare and J. Goodisman, *J. Chem. Phys.* **49** (1968) 3122.
39. G. Malli and C. Froese, *Int. J. Quant. Chem.* **15** (1967) 95.
40. Z. B. Maksić, and K. Rupnik, *Theoret. Chim. Acta* **62** (1983) 397.
41. Z. B. Maksić and K. Rupnik, *Z. Naturforsch.* **38a** (1983) 308.
42. Z. B. Maksić, *Pure Appl. Chem.* **55** (1983) 307.
43. Z. B. Maksić and J. E. Bloor, *Chem. Phys. Letters* **13** (1972) 571.
44. R. Blickensderfer, J. H. S. Wang, and W. H. Flygare, *J. Chem. Phys.* **51** (1969) 3196.
45. Z. B. Maksić, *Croat. Chem. Acta* **45** (1973) 431; Z .B. Maksić and J. E. Bloor, *J. Phys. Chem.* **77** (1973) 1520; Z. B. Maksić, *J. Mol. Structure* **20** (1974) 41; Z. B. Maksić, *Croat Chem. Acta* **48** (1976) 309.
46. Z. B. Maksić and N. Mikac, *Chem. Phys. Letters* **56** (1978) 363; Z. B. Maksić and N. Mikac, *Mol. Phys* **.40** (1980) 455.
47. J. M. Schulman and M. D. Newton, *J. Amer. Chem. Soc.* **96** (1974) 6295.
48. H. B. Jansen, A. Meeuwis, and P. Pyykkö, *Chem. Phys.* **38** (1979) 173.
49. C. Van Alsenoy, H. P. Figeys, and P. Geerlings, *Theoret. Chim. Acta* **55** (1980) 87; H. P. Figeys, P. Geerlings, P. Raeymaekers, G. Van Lommen, and N. Defay, *Tetrahedron* **31** (1975) 1731.
50. W. S. Lee and J. M. Schulman, *J. Amer. Chem. Soc.* **101** (1979) 3182; W. S. Lee and J. M. Schulman, *J. Amer. Chem. Soc.* **102** (1980) 5184.
51. N. Muller and D. E. Pritchard, *J. Chem. Phys.* **31** (1959) 768, 1471.
52. K. Frei and H. J. Bernstein, *J. Chem. Phys.* **38** (1963) 1216.
53. For an excellent review see: J. Kowalewski, *Progress in NMR Spectroscopy* **11** (1977) 1.
54. J. Wardeiner, W. Lüttke, R. Bergholz, and R. Machinek, *Angew. Chem. Int. Ed. Engl.* **21** (1982) 872.
55. W. Von Niessen, *Theoret. Chim. Acta* **27** (1972) 9.
56. J. B. Lambert, A. P. Jovanovich, and W. L. Oliver, *J. Phys. Chem.* **74** (1974) 2221.
57. K. Kamienska-Trela, *Spectrochim. Acta* **36A** (1980) 239.
58. M. Klessinger and M. Stöcker, *Org. Mag. Res.* **17** (1981) 97.
59. V. M. S. Gil and C. F. G. C. Geraldes, *J. Mag. Res.* **11** (1973) 268.
60. M. Randić and Z. Majerski, *J. Chem. Soc. B* (1968) 2389.
61. H. A. Bent, *J. Chem. Phys.* **33** (1960) 1258, 1259, 1260.
62. W. A. Bingel and W. Lüttke, *Angew. Chem. Int. Ed .Engl.* **20** (1981) 899.
63. A. D. Walsh, *Trans. Faraday Soc.* **45** (1949) 179.
64. W. A. Bernett, *J. Chem. Ed.* **44** (1967) 17.
65. J. Spanget-Larsen, R. Gleiter, M. R. Detty, and L. A. Paquette, *J. Amer. Chem. Soc.* **100** (1978) 3005; J. Spanget-Larsen, R. Gleiter, A. de Meijere, and P. Binger, *Tetrahedron* **35** (1979) 1385.
66. R. Gleiter, R. Haider, J. M. Conia, J. P. Barnier, A. de Meijere and W. Weber, *J. Chem. Soc. Chem. Comm.* (1979) 130.
67. R. Gleiter, *Topisc in Current Chemistry* **86** (1979) 199.
68. D. B. Cook, *Structures and Approximations for Electrons in Molecules,* Ellis Horwood, Chichester, 1978.
69. Z. B. Maksić, *Z. Naturforsch.* **36a** (1981) 373 and the references cited therein.
70. R. Pasternak and A. Y. Meyer, *Theoret. Chim. Acta* **43** (1977) 287.
71. A. Y. Meyer and R. Pasternak, *Theoret. Chim. Acta* **45** (1977) 45.
72. G. Del Re, *Int. Quant. Chem.* **1** (1967) 293; *ibid.* **3** (1969) 553.
73. E. F. Kirkwood and D. B. Cook, *Theoret. Chim. Acta* **44** (1977) 139.
74. K. Jug, *J. Amer. Chem. Soc.* **99** (1977) 7800.
75. M. A. Whitehead and G. D. Zeiss, *Can. J. Chem.* **61** (1983) 675.
76. R. J. Bartlett and Y. Öhrn, *Theoret. Chim. Acta* **21** (1971) 215.

SAŽETAK

Geometrija molekula. 7. Međuatomske udaljenosti, kutevi između veza i energije napetosti kod nekih rotena i sličnih spiro spojeva studiranih IMOA metodom

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Elektronska i molekulska struktura nekih tro, četvero, petero i šestero-članih prstenova rotena studirana je Iterativnom metodom maksimalnog prekrivanja. Svojstva ovih spojeva diskutirana su pomoću izračunanih hibridnih orbitala. Studirana su i svojstva koja uključuju konstante spin-spin sprezanja, termodinamičku kiselost protona kao i diamagnetski susceptibilitet.