Tetrahedron. Vol. 27, pp 6089–6099. Pergamon Press 1971. Printed in Great Britain

A COMMENT ON THE SPIROCONJUGATION THE CNDO/2 STUDIES ON THE ELECTRONIC STRUCTURES OF SOME SPIRENES AND SPIRARENES

A. TAJIRI* and T. NAKAJIMA
Department of Chemistry, Tohoku University, Sendai, Japan

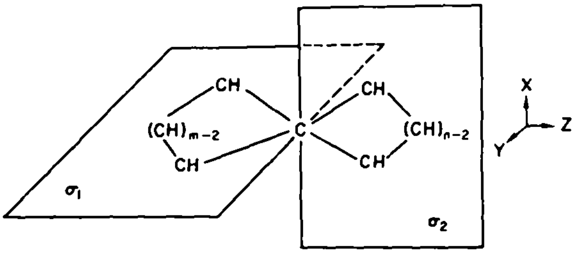
(*Received in Japan* 31 *March* 1971; *Received in the UK for publication* 2 *August* 1971)

Abstract—The equilibrium nuclear arrangements of spirenes and spirarenes in their ground states were investigated by means of the CNDO/2 method. The total energy was plotted as a function of a twisting angle θ about the central tetrahedral carbon atom for each molecule. It was found that the vertical conformation was more favourable energetically than the twisted one for each spirene. On the other hand, the twisted models were energetically stable in (3, 5)-spirarene and (5, 5)-spirarene because of the pseudo-Jahn-Teller distortion. Further, the effects of the spiroconjugation on the stabilization of the ground states were studied.

INTRODUCTION

A TERM spiroconjugation as a kind of homoconjugation[1–5] has been a useful concept for organic chemists to describe the interaction of π-systems which are separated by an insulating tetrahedral atom. Several authors have thus far been interested in the chemistry of unsaturated spirocompounds both from the experimental[6–10] and the theoretical[11–13] points of view.

Recently, Simmons and Fukunaga[11] have calculated the spectral shifts of (m/2, n/2)-spirenes (Fig. 1 and Fig. 2) using the simple Hückel MO method[14] and intensities using the molecular exciton theory,[15] and they discussed the effects of spiroconjugation on the transition energies. Hoffmann, *et al.*[12] have independently investigated the spirointeraction of (m, n)-spirarenes (Fig. 1 and Fig. 2) by use of the extended Hückel method[16] and elucidated their ground state stabilities and electronic spectra.



(m/2, n/2)-Spirene m, n ≧ 2 ; both even
(m,n) —Spirarene m, n ≧ 3 : both odd

FIG 1. Molecular structure and usual nomenclature of unsaturated spiro-compound.

---

* Present address, Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Sendai, Japan.

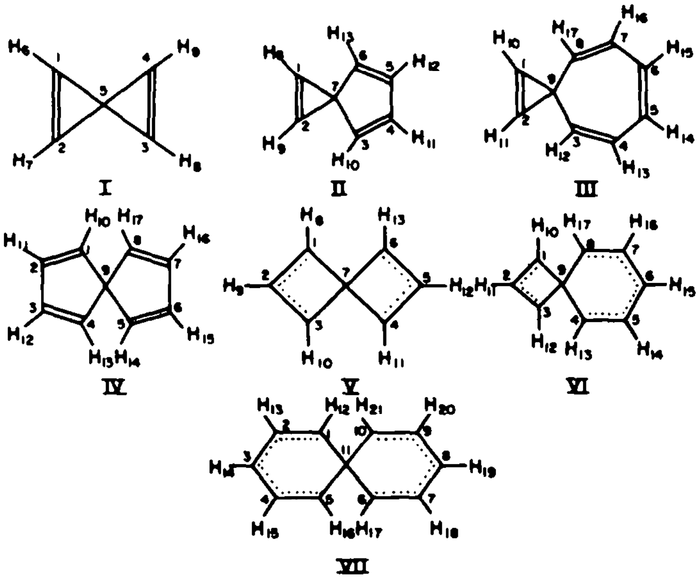


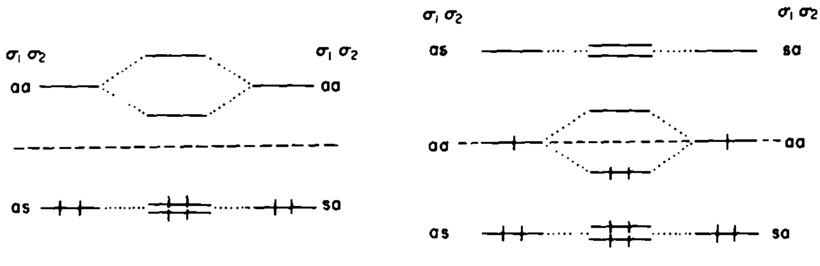
FIG 2. Nuclear arrangements and numbering of atoms of spirenes and spirarenes.

This paper is concerned with two problems. The first is what geometry makes the two π-systems interact in a most effective way that leads to the large electronic stabilization. According to the previous authors,[11–13] two planes in spirenes and spirarenes are assumed to be perpendicular to each other. This is partially supported by considering that the central carbon atoms in these molecules have rigid sp^3 tetrahedral hybridizations and that the energy difference between the sp^3 tetrahedral model and the sp^3 planar one is calculated to be 5–10 eV for CH_4.[17] It might be said that π-electron delocalization most effectively contributes to the stabilization of the ground state when the two planes lie coplanar, but the core repulsion compensates this electronic stabilization and prevents the molecule from being planar. The stable conformation of the molecule, therefore, may be established on a balance between the above two effects, electronic delocalization on the one hand and core repulsion on the other.

The second is which of the two series is more stabilized by the spiroconjugation than the other in its ground state. In spirarene each component is a polyenyl radical chain and has a nonbonding molecular orbital (NBMO), so that the spirointeraction which removes the degeneracy of these NBMO's in spirarene system is of a matter of crucial importance in determining the stability of the ground state of a molecule.

Fig. 3 shows the energy levels of two π-systems interacting in (1,1)-spirene and (3,3)-spirarene. The orbital symmetries have been determined with respect to the reflections in two perpendicular planes ($\sigma_1 = yz, \sigma_2 = xz$) containing the two fold axis (z) (Fig. 1). Introduction of the spiro-exchange interaction, which is a so-called resonance integral between the non-bonded atoms at the spiro position, leads to the stabilization of the excited state for (1,1)-spirene and of the ground state for (3,3)-spirarene.[11, 12]

As application of the MO method based on the π-electron approximation to these



(1,1)-Spirene (3,3)-Spirarene

FIG 3, π-MO interaction diagrams for (1,1)-spirene and (3,3)-spirarene.

non-planar molecules needs an empirical assumption (with inevitable ambiguities for estimation of the spiro-resonance integrals playing a very important role in determining the splittings of molecular orbitals) it is reasonable to expect that the MO method for all valence electrons can clearly make evident differences of their stability. In the CNDO/2 method,[18] electron repulsion integrals are taken into account in a semi-rigorous manner. Therefore, the CNDO/2 method is superior both to the π-electron approximation method and to the extended-Hückel method in predicting the physical and chemical properties of a molecule in its ground state. In fact, this method has predicted the equilibrium bond-lengths and angles for many polyatomic molecules in excellent agreement with the experimental values.[18b, 18c,19]

MOLECULAR ORBITAL CALCULATIONS

We apply the CNDO/2 method, without any modification of the original parameters, to these non-planar molecules. In this work, starting from the nuclear arrangements in which two planes lie perpendicularly, we vary a twisting angle θ about the tetrahedral carbon atom between 0° and 90° for each molecule, while keeping all the bond distances constant throughout the calculations;

$C(sp^3)$-$C(sp^2)$, 1·54 Å; $C(sp^2)$-$C(sp^2)$, 1·45 Å; $C(sp^2) = C(sp^2)$, 1·35 Å; $C(sp^2) \overset{\cdots}{-} C(sp^2)$, 1·45 Å; C–H, 1·00 Å. All rings are assumed to be regular polygons and H atoms are assumed to be placed radially out of the ring so that the C–H bonds are able to bisect the external CCC angles.

RESULTS AND DISCUSSIONS

Fig. 4 shows the potential energy curves plotted as a function of twisting angle θ for (1,1)-spirene (I), (1,2)-spirene (II), (1,3)-spirene (III) and (2,2)-spirene (IV). It will be seen that each spirene has a minimum point at $\theta = 0°$, and that the vertical conformation in which the two polyene rings lie perpendicularly is energetically favourable as compared with the twisted one.

Table 1 shows the distribution of electrons between the atomic orbitals, and atoms for I, II, III and IV. For II, it is clearly seen from the π-electron distributions that the smaller ring carries the positive charges and the larger one the negative. On the other hand, the total σ-electron densities on the carbon atoms show that they apparently carry the excess negative charges for the three-membered ring and positive charges for

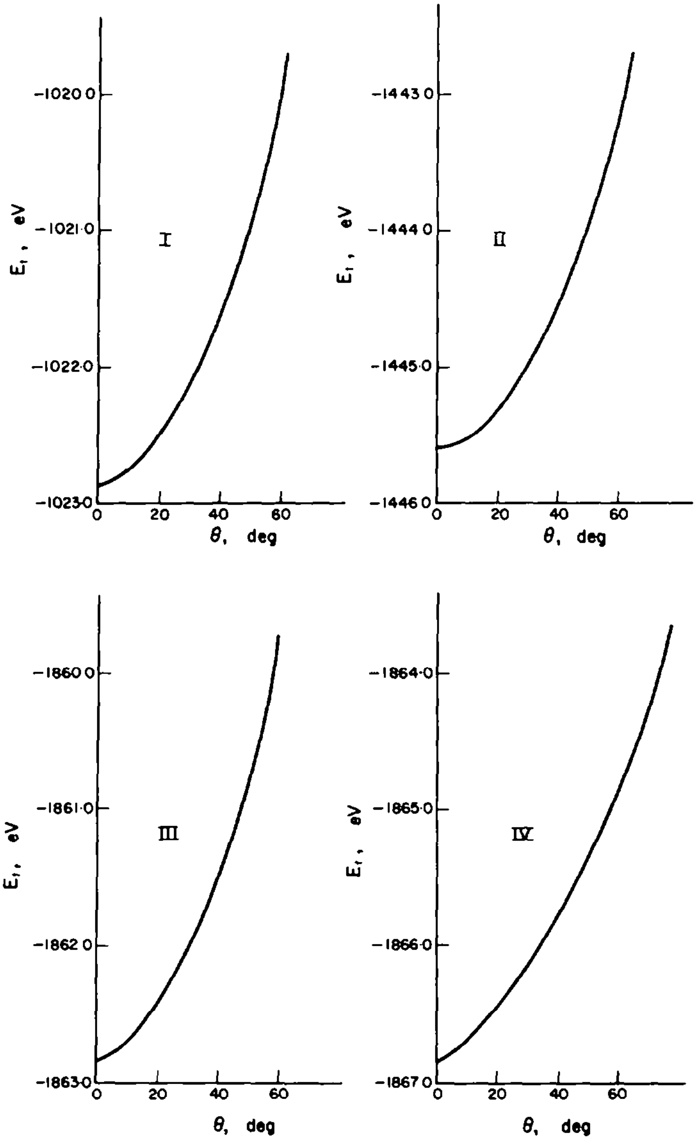


FIG 4. Total energy E_t vs twisting angle θ of spirenes.

the five-membered ring. As a result, it follows that each carbon atom in II has a fairly uniform charge distribution. The dipole moment of this molecule, however, is calculated to be 1·8D with its moment directed from the smaller ring to the larger. This appreciable dipole moment mainly arises from the charge displacement of H atoms. The total electron distributions on the unsaturated carbon atoms in III are fairly smoothed out and they give little contribution to the dipole moment of this molecule. As was shown for II the charge distributions of H atoms, however, give rise to an appreciable dipole moment for III, as large as 1·34D.

TABLE 1. AO POPULATIONS (q_{ao}) AND ATOM POPULATIONS (q_{at}) OF SPIRENES

Molecule	Atom	Orbital	q_{ao}	q_{at}
I	C_1	2s	1·010	4·058
		$2p_x$	0·967	
		$2p_y$	0·981	
		$2p_z$	1·100	
	C_5	2s	0·840	3·917
		$2p_x$	1·156	
		$2p_y$	1·156	
		$2p_z$	0·765	
	H_6	1s	0·963	0·963
II	C_1	2s	1·004	4·016
		$2p_x$	0·982	
		$2p_y$	0·981	
		$2p_z$	1·049	
	C_3	2s	1·036	4·070
		$2p_x$	0·951	
		$2p_y$	1·034	
		$2p_z$	1·050	
	C_4	2s	1·006	4·014
		$2p_x$	0·993	
		$2p_y$	1·031	
		$2p_z$	0·984	
	C_7	2s	0·931	3·931
		$2p_x$	0·988	
		$2p_y$	1·172	
		$2p_z$	0·840	
	H_8	1s	0·942	0·942
	H_{10}	1s	0·985	0·985
	H_{11}	1s	1·007	1·007
III	C_1	2s	1·004	4·032
		$2p_x$	0·983	
		$2p_y$	0·980	
		$2p_z$	1·065	
	C_3	2s	1·031	4·012
		$2p_x$	0·982	
		$2p_y$	0·976	
		$2p_z$	1·023	
	C_4	2s	1·004	4·028
		$2p_x$	0·976	
		$2p_y$	1·044	
		$2p_z$	1·005	
	C_5	2s	1·008	4·003
		$2p_x$	1·001	
		$2p_y$	1·006	
		$2p_z$	0·988	
	C_9	2s	0·923	3·948
		$2p_x$	0·949	
		$2p_y$	1·195	
		$2p_z$	0·882	
	H_{10}	1s	0·949	0·949

TABLE 1 *cont.*

Molecule	Atom	Orbital	q_{ao}	q_{at}
	H_{12}	1s	0·998	0·998
	H_{13}	1s	0·998	0·998
	H_{14}	1s	1·005	1·005
IV	C_1	2s	1·028	4·035
		$2p_x$	1·027	
		$2p_y$	0·947	
		$2p_z$	1·034	
	C_2	2s	1·010	4·008
		$2p_x$	1·023	
		$2p_y$	0·992	
		$2p_z$	0·983	
	C_9	2s	0·952	3·933
		$2p_x$	0·986	
		$2p_y$	0·986	
		$2p_z$	1·009	
	H_{10}	1s	0·974	0·974
	H_{11}	1s	1·000	1·000

Fig. 5 shows the calculated potential energy curves for (3,3)-spirarene (V), (3,5)-spirarene (VI) and (5,5)-spirarene (VII). The (3,3)-spirarene has a potential energy minimum at $\theta = 0°$. This shows that this molecule has D_{2d} symmetry and is more energetically favourable in its vertical conformation than in its twisted one. On the other hand, the minimum point of the potential energy curve is found at about $\theta = 20°$ for VI and at about $\theta = 50°$ for VII.

The stabilization energies due to the spiroconjugation which are defined to be an energy difference between the vertical structure and the twisted one are calculated to be 0·02 eV/mole—about 4·6 Kcal/mole for VI and 2·7 eV/mole—about 62·1 Kcal/mole for VII, respectively. The reason for the stable twisted conformation can be theoretically interpreted if these molecules are regarded as pseudo-Jahn-Teller molecules.[20] In Fig. 6 the interaction diagram of π-MO's is shown for (5,5)-spirarene. In the D_{2d} conformation, there appears a pair of degenerate NBMO's and the top two electrons could be placed in these orbitals in four distinct ways. In the Hückel approximation the three singlet states ($^1A_1$, $^1B_1$ and $^1B_2$) and the triplet state ($^3A_2$) are all degenerate, but when electron repulsion is included these states are split. When the molecule is twisted, the molecular symmetry is reduced from D_{2d} to D_2 and the irreducible representations of singlet states changes as follows; $^1A_1 \to {}^1A$, $^1B_1 \to A_1$ and $^1B_2 \to {}^1B_1$. Thus, in the twisted conformation, the two singlet states have the same symmetry and a strong configuration interaction occurs between these states, with the result that the twisted conformation turns out to be energetically favoured as compared with the D_{2d} conformation.

In the case of (3,5)-spirarene which belong to C_{2v} point group in its highest conformation, there is no degeneracy in molecular orbitals by symmetry. At $\theta = 0°$, however, the splitting between the HOMO and LVMO happens to be very small and they

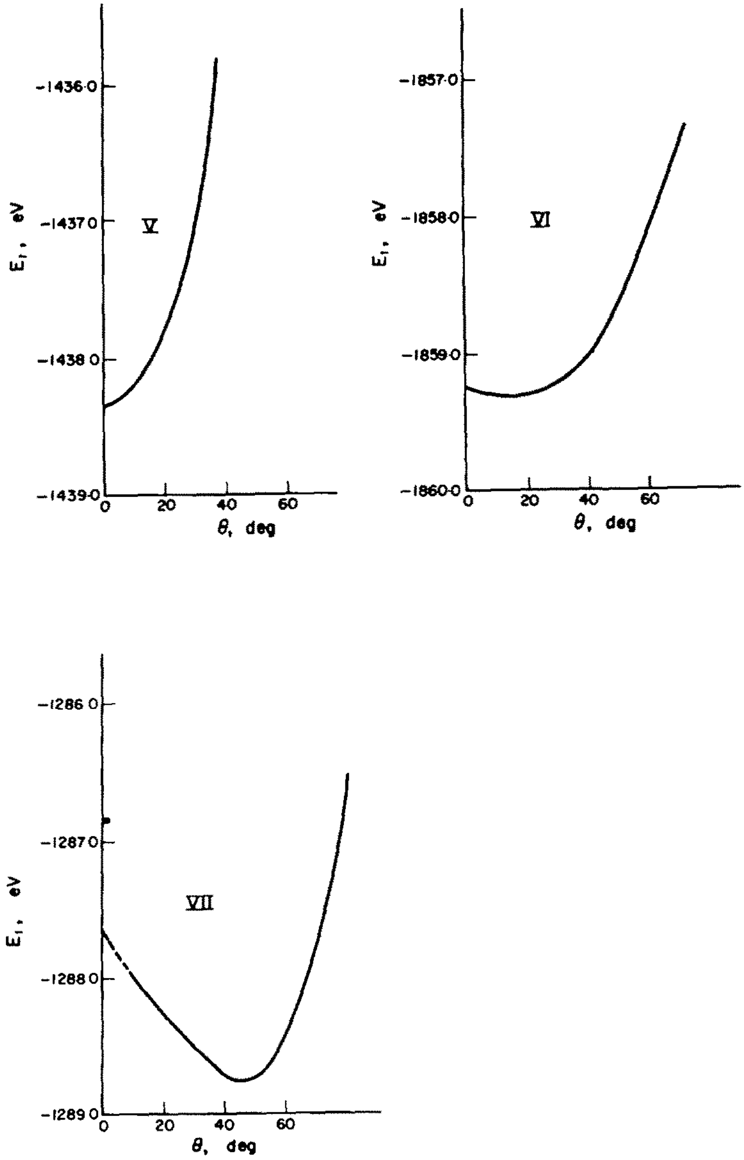


FIG 5. Total energy E_t vs twisting angle θ of spirarenes.

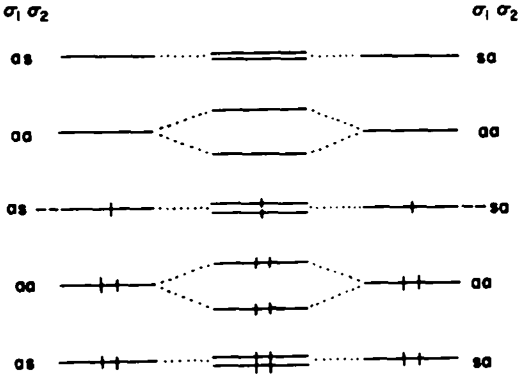


FIG 6. π-MO interaction diagram for (5,5)-spirarene.

are nearly degenerate. Therefore, one can anticipate the stabilization of the ground state of the system due to the pseudo-Jahn-Teller distortion[22c] leading to the lower C_2 symmetry than C_{2v} in this molecule.

From inspection of the interaction diagrams for higher spirarenes, we can deduce the general rules for the symmetry reduction in spirarenes as follows.

When $m = n$,

$(4q + 1, 4q + 1)$ spirarene $q = 1, 2 \ldots$ pseudo-Jahn-Teller
other spirarene not pseudo-Jahn-Teller.

When $m \neq n$,

$(4q - 1, 4r + 1)$ spirarene $q = 1, 2 \ldots (r \geqq q)$
$(4q + 1, 4r \pm 1)$ spirarene $q = 1, 2 \ldots (r > q)$ pseudo-Jahn-Teller

other spirarene not pseudo-Jahn-Teller.

The charge distributions calculated at the point corresponding to the potential energy minimum of each spirarene are summarized in Table 2 for (3,3)-, (3,5)- and (5,5)-spirarene. It is worthwhile to mention the electronic properties of (3,5)-spirarene. Carbon atoms C_1, C_3, C_5 and C_7 are strong σ-electron donors and strong π-electron acceptors, while for the other carbon atoms the situation is reversed except for the saturated central insulating carbon atom C_9. The net charge analysis shows that carbon atoms C_1 and C_3 bear σ-net charge of $+0{\cdot}252$ and π-net charge of $-0{\cdot}523$. It is found that carbon atoms C_5 and C_7 carry less positive σ-charges and less negative π-charges than those atoms on the four-membered ring. Carbon atoms C_4, C_6 and C_8 on the six-membered ring have net charges of the same order of magnitude: $-0{\cdot}14 \sim -0{\cdot}16$ for σ-net charges and $+0{\cdot}27$ for π-net charges. This displacement of charge has an effect on the direction and magnitude of the molecule's dipole moment. The charge distribution clearly shows that its dipole moment is directed from the six-membered ring to the four-membered ring. This result is inconsistent with the result concluded from the π-electron approximation[12] that a charge transfer state corresponding to $(\text{allyl})^+$ $(\text{pentadienyl})^-$ contributes to the lowest singlet electronic state. From our calculation the dipole moment of this molecule is 4·1D with the positive end at the six-membered

TABLE 2. AO POPULATIONS (q_{ao}) AND ATOM POPULATIONS (q_{at}) OF SPIRARENES

Molecule	Atom	Orbital	q_{ao}	q_{at}
V	C_1	2s	1·051	4·061
		$2p_x$	1·005	
		$2p_y$	0·917	
		$2p_z$	1·088	
	C_2	2s	1·034	4·009
		$2p_x$	1·014	
		$2p_y$	1·046	
		$2p_z$	0·915	
	C_7	2s	0·928	3·883
		$2p_x$	1·038	
		$2p_y$	1·038	
		$2p_z$	0·879	
	H_8	1s	0·968	0·968
	H_9	1s	0·990	0·990
VI	C_1	2s	0·974	4·271
		$2p_x$	1·523	
		$2p_y$	0·856	
		$2p_z$	0·917	
	C_2	2s	1·057	3·919
		$2p_x$	0·849	
		$2p_y$	1·096	
		$2p_z$	0·917	
	C_4	2s	1·078	3·889
		$2p_x$	1·047	
		$2p_y$	0·727	
		$2p_z$	1·037	
	C_5	2s	1·014	4·092
		$2p_x$	0·958	
		$2p_y$	1·133	
		$2p_z$	0·987	
	C_6	2s	1·075	3·876
		$2p_x$	1·045	
		$2p_y$	0·737	
		$2p_z$	1·019	
	C_9	2s	0·948	3·880
		$2p_x$	0·875	
		$2p_y$	1·059	
		$2p_z$	0·998	
	H_{10}	1s	0·987	0·987
	H_{11}	1s	1·018	1·018
	H_{13}	1s	0·957	0·957
	H_{14}	1s	0·972	0·972
	H_{15}	1s	0·971	0·971
VII	C_1	2s	0·967	3·954
		$2p_x$	1·060	
		$2p_y$	1·009	
		$2p_z$	0·918	
	C_2	2s	1·031	4·044
		$2p_x$	1·003	

TABLE 2 *cont.*

Molecule	Atom	Orbital	q_{ao}	q_{at}
		$2p_y$	1·017	
		$2p_z$	0·994	
	C_3	2s	1·032	4·139
		$2p_x$	1·049	
		$2p_y$	1·083	
		$2p_z$	0·975	
	C_{11}	2s	0·899	3·860
		$2p_x$	0·848	
		$2p_y$	0·948	
		$2p_z$	1·166	
	H_{12}	1s	0·989	0·989
	H_{13}	1s	0·983	0·983
	H_{14}	1s	0·990	0·990

ring. It is undoubtedly apparent that the contribution of the $(\text{allyl})^-$ $(\text{pentadienyl})^+$ state is fairly large in its ground electronic state.

Throughout the tables, the central tetrahedral carbon atoms carry the more positive charges than the other carbon atoms in the rings, as is qualitatively expected from the differences in the hybridization of two types of carbon atoms; sp^2 on the one hand, and sp^3 on the other.[21]

We have seen above that some spirarenes are more energetically stable in the twisted conformation than in the vertical one, while all spirenes have energy minima at $\theta = 0°$. The results on the stable nuclear arrangements for spirenes and spirarenes make one think that a difference exists in the spirointeraction between the two systems. We here introduce a term "spiro-bondorder", a long range bondorder between the non-bonded atoms at spiro positions. In the molecular orbital calculations including all valence electrons explicitly there are so many interactions, as many as sixteen even if we consider only two atoms at spiro positions, that it is assumed that we only consider the spiro-bondorders between $2p\pi$AO's of the rings as a first approximation.

The spiro-bondorders of spirenes and spirarenes calculated at the potential energy minimum point are summarized in Table 3. It will be seen that there is apparently clear cut-off in the spiro-bondorders between spirenes and spirarenes. The spiro-bondorders of spirenes are small (0·00 for (1, 1)-spirene, 0·038 for (1, 2)-spirene, 0·026

TABLE 3. SPIRO-BONDORDERS P_{spiro} OF SPIRENES AND SPIRARENES

Spirenes		P_{spiro}	Spirarenes		P_{spiro}
I	1–3	0·00	V	1–4	0·50
II	1–3	0·04	VI	1–4	0·14
				1–8	0·12
III	1–3	0·03	VII	1–6	0·12
				1–10	0·09
IV	1–5	0·04			

for (1,3)-spirene and 0·024 for (2,2)-spirene) as compared with those of the spirarenes (0·500 for (3,3)-spirarene, 0·119 (C_1–C_8) and 0·144 (C_1–C_4) for (3,5)-spirarene and 0·093 (C_1–C_{10}) and 0·115 (C_1–C_6) for (5,5)-spirarene). Therefore, it is concluded from the analysis of the spiro-bondorders that the long range spirointeraction (spiroconjugation) through an insulating tetrahedral carbon atom is more pronounced in spirarenes than in spirenes.

CONCLUSIONS

It is concluded from the CNDO/2 calculations that the equilibrium nuclear arrangements of (1,1)-, (1,2)-, (1,3)- and (2,2)-spirene, and also (3,3)-spirarene in their ground state are such that the two constituent polyene and polyenyl radical rings are joined perpendicularly through the tetrahedral carbon atoms. As for the stable nuclear conformations of (3,5)- and (5,5)-spirarene it is found that the former has a potential energy minimum at $\theta = 20°$ and the latter at $\theta = 50°$, which may be interpreted as due to the pseudo-Jahn-Teller distortion.

Furthermore, it is apparent from the discussion of spiro-bondorders that a clear-cut difference exists in spiroconjugation effect between them; the spiro-bondorders of spirarenes are greater than those of spirenes. The spiro-bondorder shows, however, that its magnitude is small compared with that of aromatic molecules and that spiroconjugation has a little contribution, if any, to the stabilization of the molecules in their ground states.

REFERENCES

[1] A. Winstein and R. Adams, *J. Am. Chem. Soc.* **70**, 838 (1948)

[2] S. Winstein and A. H. Schlesinger, *Ibid.* **70**, 3528 (1948)

[3] S. Winstein, H. M. Walborsky and K. Schreiber, *Ibid.* **72**, 5795 (1950)

[4] M. Simonetta and S. Winstein, *Ibid.* **76**, 18 (1954)

[5] S. Winstein, *Quart. Rev.* **23**, 141 (1969)

[6] D. J. Cram and B. L. Van Durren, *J. Am. Chem. Soc.* **77**, 3576 (1955)

[7] E. T. McBee, G. W. Calundann and T. Hodgins, *J. Org. Chem.* **31**, 4260 (1966)

[8] M. Jones, Jr., *Ibid.* **33**, 2538 (1968)

[9] D. Schonleber, *Angew. Chem.* **81**, 83 (1969)

[10] D. Schonleber, *Chem. Ber.* **6**, 1789 (1969)

[11] H. E. Simmons and T. Fukunaga, *J. Am. Chem. Soc.* **89**, 5208 (1967)

[12] R. Hoffmann, A. Imamura and Z. D. Zeiss, *Ibid.* **89**, 5215 (1967)

[13] R. Boschi, A. S. Dreiding and E. Heilbronner, *Ibid.* **92**, 123 (1970)

[14] A. Streitwieser, Jr., *Molecular Orbital Theory for Organic Chemists* p. 33, John Wiley and Sons, Inc., New York, London (1963)

[15] J. N. Murrel, *The Theory of the Electronic Spectra of Organic Molecules* p. 136, John Wiley and Sons, Inc., New York, N.Y. (1963)

[16] R. Hoffmann, *J. Chem. Phys.* **39**, 1397 (1963)

[17] [a] R. Hoffmann, R. W. Alder and C. Wilcox, Jr., *J. Am. Chem. Soc.* **92**, 4992 (1970); [b] H. J. Monkhorst, *Chem. Commun.* 1111 (1968)

[18] [a] J. A. Pople, D. P. Santry and G. A. Segal, *J. Chem. Phys.* **43**, s129 (1965); [b] J. A. Pople and G. A. Segal, *Ibid.* **43**, s136 (1965); [c] J. A. Pople and G. A. Segal, *Ibid.* **44**, 3289 (1966)

[19] [a] G. A. Segal, *J. Chem. Phys.* **47**, 1876 (1967); [b] K. B. Wiberg, *J. Am. Chem. Soc.* **90**, 59 (1968)

[20] [a] H. A. Jahn and E. Teller, *Proc. Roy. Soc.* (London), **A161**, 220 (1937); [b] L. C. Snyder, *J. Chem. Phys.* **62**, 2299 (1962); [c] C. A. Coulson, *J. Chem. Soc. Spec. Publ.* No. 12, p. 85 (1958)

[21] C. A. Coulson, *Valence* p. 206, Oxford University Press, London (1952)