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BOND LENGTH ALTERNATION IN *s*-INDACENE

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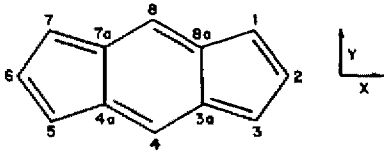
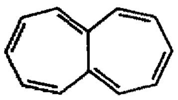
Abstract—Using a modification of the Hückel MO theory, it is shown that in the *s*-indacene molecule the peripheral C—C bonds alternate considerably in length, and the skew structure (C_{2h}) is energetically favoured as compared with the conventional symmetric one (D_{2h}). The charge densities and free valence numbers in the skew structure indicate that the molecule should be highly reactive. It is found that the bond length alternation strongly reduces such quantities indicative of π-electron delocalization as the delocalization energy and the diamagnetic anisotropy. The energies and moments for the lower electronic transitions are also calculated. The result is in agreement with the experimental fact that the molecule is red. All the above results agree that *s*-indacene should have very little aromatic character.

INTRODUCTION

RECENTLY Hafner *et al.*[1] have reported the successful synthesis of the nonbenzenoid aromatic hydrocarbon *s*-indacene $C_{12}H_8$ (I) and discussed its aromatic characteristics. The new compound consisting, so to speak, of the addition of the two fulvene molecules has been of interest since it was first postulated as a possible aromatic system by Brown[2] in 1951. From the viewpoint of the molecular-orbital theory *s*-indacene is closely related to the recently prepared[3] heptalene $C_{12}H_{10}$ (II). Both these molecules are considered as formed by the introduction of certain cross-links into the cyclic polyene $C_{12}H_{12}$, and belong, according to Craig's classification,[4] to a special class of compounds known as the pseudo-aromatics.



I



II

Using molecular-orbital theory den Boer-Veenendaal *et al.*,[5] Snyder[6] and Nakajima *et al.*[7,8] have recently shown that heptalene should possess the C—C bonds of alternating lengths along its periphery. In other words, a structure of the

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[1] K. Hafner, K. H. Häfner, C. König, M. Kreuder, G. Ploss, G. Schulz, E. Sturm and K. H. Vöpel, *Angew. Chem.* **75**, 35 (1963); K. Hafner, *Ibid.* **75**, 1041 (1963).

[2] R. D. Brown, *J. Chem. Soc.* 2391 (1951).

[3] H. J. Dauben and D. J. Bertelli, *J. Amer. Chem. Soc.* **83**, 4659 (1961).

[4] D. P. Craig and A. Maccoll, *J. Chem. Soc.* 964 (1949); D. P. Craig, *Theoretical Organic Chemistry* p. 20. Butterworths, London (1959).

[5] P. C. den Boer-Veenendaal, J. A. Vliegenthart and D. H. W. den Boer, *Tetrahedron* **18**, 1325 (1962).

[6] L. C. Snyder, *J. Phys. Chem.* **66**, 2299 (1962).

[7] T. Nakajima and S. Katagiri, *Mol. Phys.* **7**, 149 (1963).

[8] T. Nakajima, Y. Yaguchi, R. Kaeriyama and Y. Nemoto, *Bull. Chem. Soc. Japan* **37**, 272 (1964).

familiar D_{2h} symmetry should be less favourable energetically than one exhibiting molecular symmetry C_{2h}. A re-examination of the same problem from the valency-bond point of view by den Boer *et al.*[9] has also confirmed this result. The possible occurrence of a less symmetric configuration in heptalene, if it is treated as the slightly perturbed hypothetical cyclic polyene $C_{12}H_{12}$, may be ascribed to a pseudo-Jahn-Teller effect.[10] If the same approach is followed for *s*-indacene, a similar behaviour may appear. The purpose of this paper is to determine the equilibrium configuration of *s*-indacene with respect to bond length distortion using a modification of the Hückel MO method and to examine theoretically its ground-state electronic properties and electronic spectrum. It should be possible to use the results of such calculations to deepen our understanding of the aromatic characteristics of this molecule.

THE BOND LENGTH ALTERNATION

The method employed in determining the equilibrium bond length alternation is a minimum energy method described previously,[7] one in which the effects of the σ-bond compression,[11,12] now recognized to be of supreme importance in such a problem, have been properly taken into consideration. The total binding energies V, taken to be the sum of π-bond energy and σ-bond energy, are calculated for a series of values varying from 0 to 1 of the bond alternation parameter k defined as

$$k = \beta_s/\beta_d \qquad (1)$$

where β designates the resonance integral parameter and the subscripts s and d mean the single and double bonds in an unexcited Kekulé structure, respectively. Thus the equilibrium bond alternation k_{min} is given by a minimum of the V–k curve.

It may be added that the minimum energy method above has been successfully used to account for the equilibrium configurations of the fundamental nonbenzenoid aromatic hydrocarbons, such as the fulvenes, the fulvalenes, pentalene and heptalene.[13]

The V–k curve for *s*-indacene is shown in Fig. 1. The k_{min} value turns out to be 0·59, which indicates that in *s*-indacene there exists a significant bond length alternation, one comparable in extent to those in heptalene (with $k_{min} = 0{\cdot}58$) and butadiene (with $k_{min} = 0{\cdot}55$).[7] The deformation energy which favours the bond length distortion is estimated to be $-0{\cdot}26\,\beta_0$*—about 4 kcal/mole (cf. heptalene, about 7 kcal/mole[13]), if we take $\beta_0 = -16{\cdot}5$ kcal/mole (see below)—which is an appreciable amount.

The bond length alternation in *s*-indacene, if it is treated as the slightly perturbed hypothetical planar cyclododecahexaene may be related to the open-shell configuration owing to the degeneracy of the top occupied orbitals (a pseudo-Jahn–Teller

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* The standard β_0 is β for the case $k = 1$, namely, for benzene.

[9] P. C. den Boer, D. H. W. den Boer, C. A. Coulson and T. H. Goodwin, *Tetrahedron* **19**, 2163 (1963).

[10] C. A. Coulson, *J. Chem. Soc. Spec. Publ.* No. 12. p. 85 (1958).

[11] H. C. Longuet-Higgins and L. Salem, *Proc. Roy. Soc.* **A251**, 172 (1959).

[12] C. A. Coulson and W. T. Dixon, *Tetrahedron* **17**, 215 (1962).

[13] T. Nakajima, *Molecular Orbitals in Chemistry* (Edited by B. Pullman and P. O. Löwdin) Academic Press, New York, in press.

effect).[10] In *s*-indacene, however, using the Hückel MO method (with $k = 1$), no such a genuine degeneracy is found. Nevertheless, it may be said that the molecule has a pseudo-open-shell configuration in the sense that it has a vacant nonbonding orbital. On the other hand, in the distorted structure (C_{2h}) here obtained all the vacant orbitals were found to be antibonding. The asymmetric distortion of the nuclear framework results in the achievement of a closed electron shell. Such rearrangements of the molecular orbitals are demonstrated by the data of Table 1.

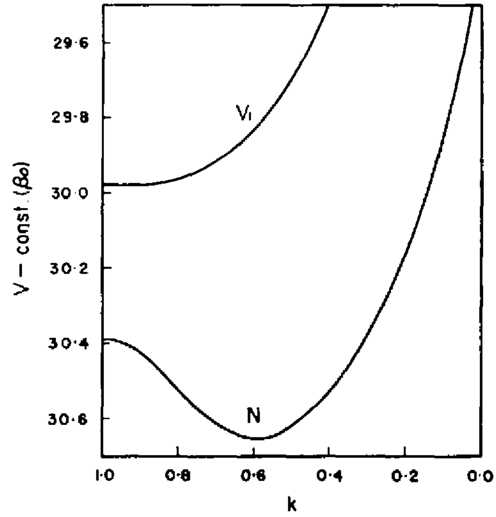

FIG. 1. The V–k curve for *s*-indacene. Curve N, the ground state; curve V_1, the lowest excited state.

TABLE 1. ENERGIES AND SYMMETRY ASSIGNMENTS OF MOLECULAR ORBITALS OF *S*-INDACENE*†

Perimeter	D_{2h}	C_{2h}
−2·000	−2·303 b_{3g}	−1·718 b_g
−1·732	−1·757 b_{1u}	−1·437 a_u
−1·732	−1·618 b_{2g}	−1·320 b_g
−1·000	−1·618 a_{1u}	−1·214 a_u
−1·000	−0·820 b_{1u}	−0·762 a_u
0	0 b_{3g}	−0·255 b_g
0	0·618 a_{1u}	0·624 a_u
1·000	0·618 b_{2g}	0·630 b_g
1·000	1·139 b_{1u}	0·954 a_u
1·732	1·303 b_{2g}	1·128 b_g
1·732	2·000 b_{3g}	1·535 b_g
2·000	2·438 b_{1u}	1·835 a_u

* The energies are characterized by the coefficients c in $E = \alpha + c\beta$.

† In the upper half of the Table are tabulated vacant orbitals in the ground state and in the lower half are tabulated occupied orbitals.

Finally it is of interest to mention the bond length distortion in the dianion of *s*-indacene which has been known to be reasonably stable.[1] If the same approach as applied to the neutral system is straightforwardly followed for the dianion, the $k_{\min}$ value turns out to be 0·95. The dianion shows very little if any bond length alternation.

CHARGE DENSITIES, BOND ORDERS AND FREE VALENCES

The charge densities, bond orders and free valence numbers for the asymmetric (C_{2h}) structure are summarized in Table 2. It should be noted that the charge densities and the free valence numbers (of the secondary carbon atoms) are considerably smoothed out as compared with those[2] obtained using the simple Hückel method (with $k = 1$). The charge densities are distinctly lowest at positions 4 and 8. This indicates that the highest reactivity for nucleophilic reaction is to be expected at these positions, the prediction being in agreement with available experimental facts.[1] From the viewpoint of chemical reactivity, it is particularly noteworthy that the free valences of the secondary carbon atoms are all significantly larger than those in classical aromatic hydrocarbons (e.g., benzene, 0·40). The hydrocarbon is thus expected to be highly susceptible to homolytic reactions. This perhaps provides one of the reasons for the enormously great instability of this molecule.*

TABLE 2. CHARGE DENSITIES, FREE VALENCES AND BOND ORDERS

Atom	Charge density	Free valence	Bond	Bond order
1	1·014	0·535	1–2	0·908
2	1·030	0·507	1–8a	0·289
3	0·984	0·555	2–3	0·318
4	0·906	0·552	3–3a	0·859
3a	1·032	0·267	4–3a	0·309
8a	1·032	0·276	8–8a	0·871
			3a–8a	0·296

THE DELOCALIZATION ENERGY

The magnitude of the π-electron delocalization energy *DE* or the *DE* per π electron has occasionally been used as an auxiliary criterion for aromaticity.

The *DE* for *s*-indacene defined as the difference in π-electron energy between the equilibrium configuration (with $k = 0{\cdot}59$) and the nonresonating Kekulé structure (with $k = 0$) is calculated to be $-1{\cdot}73\,\beta_0$. If we use $\beta_0 = -16{\cdot}5$ kcal/mole that best fits the empirical resonance energies for a group of benzenoid[3] and non-benzenoid[13] aromatic hydrocarbons, a *DE* value of 29 kcal/mole (cf. heptalene, 24 kcal/mole[13]) results. This figure is considerably lower than the *DE* (70 kcal/mole) obtained for the symmetric (D_{2h}) model with $k = 1$. The *DE*/electron value is $-0{\cdot}14\,\beta_0$ (cf. heptalene, $-0{\cdot}12\,\beta_0$[13]), which is significantly small as compared with those for benzenoid aromatic hydrocarbons (e.g., benzene, $-0{\cdot}33\,\beta_0$).

It is interesting to add in this connection that the *DE*/electron for the dianion of

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* The authors wish to thank Professor K. Hafner for providing us with this information.

s-indacene is calculated to be $-0{\cdot}45\ \beta_0$, which is comparable to those for classical aromatic hydrocarbons.

MAGNETIC PROPERTIES

One of the important quantities indicative of the π-electron delocalization of an aromatic compound is the magnetic susceptibility attributed to induced ring currents in its π-electron network. The method employed for the theoretical estimate of the molar magnetic anisotropy of *s*-indacene is Hoarau's modification[14] of the London technique:

$$\Delta K = (\tfrac{1}{3})\Delta K_{\mathrm{London}} + 0{\cdot}776 \times 10^{-18} DE \tag{2}$$

The calculated ΔK values in unit of $\Delta K_{\mathrm{benzene}}$ for the symmetric (D_{2h}) and asymmetric (C_{2h}) models are $-0{\cdot}66$ and $0{\cdot}028$, respectively. It is seen how sensitive the magnetic anisotropy is to the extent of bond alternation; the magnetic anisotropy is calculated to be paramagnetic (a quenched paramagnetism[15]) when $k = 1$ and turns out to be diamagnetic when $k = 0{\cdot}59$. The figure for the asymmetric model indicates that in *s*-indacene the diamagnetically induced ring currents should be impeded considerably. A part of evidence of this conclusion is given by the NMR spectrum of this molecule,[1] which indicates that in it the π-electron delocalization should be fairly restricted. For heptalene the $\Delta K/\Delta K_{\mathrm{benzene}}$ value was calculated to be $-0{\cdot}21$.[13] This implies that the proton signals of *s*-indacene should appear at lower fields than do those of heptalene. Actually *s*-indacene exhibits signals between 2·4 and 3·7 τ[1] and heptalene between about 4 and 5 τ.[3]

It is added that the dianion of *s*-indacene with $\Delta K/\Delta K_{\mathrm{benzene}} = 2{\cdot}6$ exhibits a normal diamagnetism like those in benzenoid systems.

THE ELECTRONIC SPECTRUM

The electronic transition energies are calculated, electron interaction terms being taken into account using the semiempirical method of Pariser and Parr.[16] In computing interaction terms for adjacent atoms, the bond orders were used to predict the bond lengths. However, nonneighbour internuclear distances were calculated assuming the rings to be regular, with the bond lengths taken to be 1·397 Å. The one-center electronic repulsion integral given in the Pariser and Parr formulation as $I_c - A_c$ was taken to be $11{\cdot}54 - 0{\cdot}46 = 11{\cdot}08$ eV,[17] and the two-center repulsion integrals were obtained using the normal extrapolation procedure of Pariser and Parr. Orbital energies are computed in units of β_d in the present procedure. We adopt a value of $-6{\cdot}96$ eV* as the β_d for the asymmetric *s*-indacene with $k_{\min} = 0{\cdot}59$.

In *s*-indacene, if it is distorted in the asymmetric (C_{2h}) manner, a configuration interaction is possible between the ground state and the lowest excited state, since the symmetry representations of the two states are both A_g in the distorted structure.

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* The β_d value for $k = 0{\cdot}55$ was adjusted so as to reproduce the observed energy of the lowest singlet transition (5·9 eV) of butadiene, and was found equal to $-7{\cdot}10$ eV. Using this value, we found the β_d value for $k = 1$ to be $-5{\cdot}51$ eV.[7] A linear relationship between β_d and k was then assumed to obtain β_d values for various k values. Thus, we found $\beta_d = -6{\cdot}96$ eV for $k = 0{\cdot}59$.

[14] J. Hoarau, *Ann. Chim.* **1**, 544 (1956).

[15] G. Wagnière and M. Gouterman, *Mol. Phys.* **5**, 621 (1962).

[16] R. Pariser and R. G. Parr, *J. Chem. Phys.* **21**, 466, 767 (1953).

[17] H. D. Pritchard, *Chem. Rev.* **52**, 529 (1955).

Insofar as the distortion remains slight, the interaction may be of primary importance, and heavy mixing of the two states will occur, the ground state being substantially depressed in energy.[18] However, in the distorted structure here achieved the interaction is of little importance, for the two states are well separated in energy from each other. Actually the lowering of the ground-state energy caused by the interaction is calculated to be 0·25 eV. The minimum energy method here employed considerably reduces the effects of the configuration interaction.

The calculated energies and oscillator strengths f for the lower singlet electronic transitions are presented in Table 3. The lowest allowed singlet transition is predicted to be polarized approximately along the long axis (x), whereas the next allowed weaker transition is predicted to be polarized roughly along the short axis (y). The forbidden transition predicted to be lowest in energy, if it is partially allowed by molecular vibrations or twistings, will be observed as a long weak absorption tail, which accompanies the longest-wavelength allowed transition, throughout the visible. The reason is because the potential energy (V–k) curve for the excited state of this transition differs considerably in shape from that for the ground state, the former having a single potential energy minimum, whereas the latter has a double minimum (Fig. 1). A quite similar long absorption tail has been predicted[13] and actually observed in heptalene.[3]

TABLE 3. PREDICTED SINGLET ELECTRONIC TRANSITIONS

Transition type	Excitation energy (eV)	f (cgs)
$A_g \leftarrow A_g$	1·75	Forb.
$B_u \leftarrow A_g$	2·70	0·43
$B_u \leftarrow A_g$	4·53	0·20

No experimental spectral data of s-indacene are available at present. However, the results of the present spectral calculations are not incompatible with the fact that it has a red colour.

CONCLUSION

All the above results agree that the s-indacene molecule exhibits a marked alternation in length in its peripheral C—C bonds and the molecular symmetry group for it is C_{2h} instead of D_{2h}. In conclusion, we can say that the hydrocarbon has very little, if any, aromatic stability from the viewpoint of π-electron delocalization and also from the viewpoint of chemical reactivity. It should have characteristics of a cyclic polyolefin. In many respects, s-indacene is very similar to heptalene, though π-electron delocalization effects in the former are somewhat enhanced as compared with those in the latter.

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[18] H. C. Longuet-Higgins, *Theoretical Organic Chemistry* p. 9. Butterworths, London (1959).