mass spectrum, m/e (relative intensity) 187 (6), 171 (5), 173 (5), 163 (10), 162 (100), 132 (8), 78 (7), 58 (10). Anal. Calcd for C16H28NO5: C, 68.41; H, 8.04; N, 5.66. Found: C, 68.22; H, 7.80; N, 5.66. The other diastereoisomer of 4m, m/e 155–155 °C; showed: IR (CHCl3) 3360, 1700 cm−1; NMR (CDCl3) δ 5.00 (s, 3 H), 1.16 (d, J = 7 Hz, 3 H), 1.37 (s, 3 H), 3.11 (s, 3 H), 3.58 (s, 3 H), 3.81 (q, J = 7 Hz, 1 H), 5.80 (s, 1 H), 7.30–7.92 (m, 4 H); mass spectrum, m/e (relative intensity) 187 (6), 172 (6), 183 (13), 162 (100), 133 (6), 70 (6), 59 (10), 55 (15). Anal. Calcd for C16H28NO5: C, 68.41; H, 8.04; N, 5.66. Found: C, 68.59; H, 8.36; N, 5.15.


Is Bicyclo[6.2.0]decapentaene Aromatic or Antiaromatic?

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Charles W. Bock

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Received December 14, 1984

Ab initio HF/STO-3G and MNDOC calculations on bicyclo[6.2.0]decapentaene (1) suggest that it possesses a slightly puckered equilibrium structure with C1 symmetry. The barrier to planarity is, however, lower than room temperature, i.e., 1 is at room temperature T essentially planar. According to theory, there is some peripheral delocalization of π electrons leading to weak aromaticity of 1. The calculated resonance energy of 1 is 4 kcal/mol. There exist two valence tautomers of 1 which are 11 and 23 kcal/mol less stable than 1. MNDOC calculations indicate that both forms easily undergo bond shifting and, therefore, are hardly detectable if not stabilized by benzoannelation.

The electronic nature of bicyclo[6.2.0]decapentaenes has attracted considerable interest by both experimentalists' and theoreticians, in particular after the first successful synthesis of the parent compound (1, see Scheme I) by Oda and co-workers. 1 contains in its periphery four π electrons which should lead to some aromatic stabilization. This electronic stabilization, however, may be compensated by potential antiaromatic character of the component rings of 1 which are 4n π electron systems. Destabilization will increase if forms 2 and 3 (Scheme I) contribute substantially to the electronic structure of 1. Simple HMO or graph theoretical considerations predict a preponderance of the antiaromatic character of the component rings of 1. These predictions have recently been supported by results of an elaborate MOP2 force field investigation of 1 carried out by Allinger and Yuh. By making an as-


The results of the MNDO study on bicyclo[6.2.0]decapentaene (1) have been published in J. Am. Chem. Soc. 1983, 1000–1007; Angew. Chem., Int. Ed. Engl. 1983, 22, 1003–1004. These predictions have recently been supported by results of an elaborate MOP2 force field investigation of 1 carried out by Allinger and Yuh. By making an as-

Figure 1. Ab initio (HF/STO-3G) and MNDOC (in parentheses) structural parameters of C4, symmetrical 1. Since parameters, which would be related by symmetry in the C4 form of 1, possess similar values, only their average is given. (a) Bond lengths (Å). (b) Bond angles. (c) Absolute values of dihedral angles. (d) Torsions are confined to CC single bonds, i.e., is only considered to be equal. Of these forms only the trans form with folding angles of 15° and 110° (MNDO) has been considered to be equal. 

We now wish to report on the electronic structure of 1 as obtained by ab initio calculations (HF/STO-3G) and complemented by extensive MNDO and MNDOC calculations both on 1 and the related forms 2-7 (see Scheme 1). Our investigation is aimed at solving the contradiiction between theoretical and experimental results and providing evidence as to the existence of 2 or 3 as possible valence tautomeric forms of 1. For this purpose we have determined equilibrium geometry, puckering potential, heat-of-formation, resonance energy, and electron density distribution ρ(r) of 1. Special emphasis is laid on an appropriate analysis of the latter in order to obtain CC bond orders α and bond ellipticities ε.20 As has been recently shown, both quantities allow a description of the degree of π-electron delocalization in a conjugated system.3

Computational Details. Employing gradient and quasi-Newton methods with an analytical determination of energy derivatives, complete geometry optimization of forms 1-7 have been carried out within the following symmetrical and geometrical constraints: 1: C4 symmetry; optimization of all 3(18) - 6 = 48 geometrical parameters; at the ab initio level the eight CH bond lengths have been fixed at a value of 1.08 Å. 2, 3, and 4: C4 symmetry; the

<table>
<thead>
<tr>
<th>HF/ parameter</th>
<th>STO-3G</th>
<th>expb</th>
<th>MNDOC</th>
<th>MNDO</th>
<th>MMP2</th>
</tr>
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<tr>
<td>R(1,2)</td>
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<td>1.330</td>
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<td>1.341</td>
<td>1.342</td>
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<tr>
<td>R(2,3)</td>
<td>1.482</td>
<td>1.455</td>
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</tr>
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<td>1.355</td>
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</table>

Results and Discussions

In Figure 1, averaged bond lengths, averaged bond angles, averaged dihedral angles, and the folding angles α and β of C4 symmetrical 1 are shown as obtained at the ab initio level of theory. Calculated MNDOC parameters (in parentheses) are also depicted in Figure 1. Theoretical bond lengths and folding angles are compared with relevant data from other sources in Table I. An analysis of these values leads to the following results.

(1) The eight-membered ring of 1 adopts a shallow tub form with folding angles of 15° and 11° (MNDO). The corresponding ab initio values are somewhat smaller but both levels of theory suggest that 1 is slightly puckered. Torsions are confined to CC single bonds, i.e., possesses C4 symmetry rather than C2, symmetry (see Figure 1 part d). The actual deviation from C4 symmetry is, however, rather small.

(2) According to both ab initio and MNDO theory the barrier to planarity is lower than 0.6 kcal/mol, i.e., the puckering potential is flat with a small hump at α = β = 0°. At room temperature 1 can adopt folding angles between 30° and -30°, i.e., on average the bicyclic system is essentially planar. This is in line with Oda’s observation that the actual conformation of 1 is highly sensitive to the influence of substituents, crystal forces, and other environmental effects.

(3) The calculated central bond length (C1-C4) is rather long (1.528 Å, ab initio; 1.514 Å MNDOC) in agreement with the X-ray value for the 9,10-diphenyl derivative of 1 (1.535 Å) but contrary to the MMP2 force field result (1.475 Å).

(4) Calculated bond lengths reveal that the degree of bond alternation is somewhat smaller in 1 than, e.g., in trans-1,3-butadiene (Table 1). MNDO (MNDOC) values are in good agreement with experimental data while ab initio values differ on the average by 0.04 Å. The latter

7 Bond lengths in Å. 8 Averaged values of the X-ray investigation of 9.10-diphenylbicyclo[6.2.0]decapentaene from ref 7. Due to the influence of the substituents the 9,10-bond is lengthened. 9 Force field calculations from ref 6. 10 Almenningen, A.; Bastiansen, O.; Traetteberg, M. Acta Chem. Scand. 1985, 12, 1221. 11 Kao, J.; Al linger, N. L. J. Am. Chem. Soc. 1977, 99, 975. CC bond lengths of the four-membered ring of 4 have been considered to be equal. 5, 6, and 7: C2v; symmetry; planarity assumed; all peripheral CC bonds of 5, all CC bonds of the eight-membered ring of 6, and all CC bonds of the four-membered ring of 7 have been considered to be equal. 5, 6, and 7: C2v; symmetry; planarity assumed; all peripheral CC bonds of 5, all CC bonds of the eight-membered ring of 6, and all CC bonds of the four-membered ring of 7 have been considered to be equal. Of these forms only 1, 2, 3 are located at minima of the MNDO or the (correlation-corrected) MNDOC energy hypersurface of bicyclo[6.2.0]decapentaene.

Table I. Comparison of Theoretical and Experimental Structural Data of 1 and trans-1,3-Butadienea

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observation, however, is not surprising in view of the known deficiencies of the STO-3G basis when applied to cyclopolyenes.12

A direct assessment of the degree of electron delocalization in 1 is provided by an analysis of the computed total electron density distribution \( \rho(r) \). Using ethylene as the appropriate reference molecule, we define the \( \pi \) character of a CC bond (in percent) by the ratio \( \eta = 100 \times t^{(CC)}/t^{(ethylene)} \) where the bond ellipticity \( t \) measures the anisotropy of \( \rho(r) \) at a CC bond.15 The value of \( \eta \) is large if the \( \pi \) character of a CC bond is fully established (\( \eta \) (ethylene) = 100%) while it is zero for a CC bond without any \( \pi \) contributions.

Our results suggest that the 1,8-bond of 1 possesses only low \( \pi \) character (\( \eta < 10\% \), see Figure 2). According to calculated bond orders \( n \) and bond ellipticities \( \epsilon (\pi \text{ character } \eta) \), delocalization of \( \pi \) electrons occurs essentially along the periphery of the bicyclic system. The \( \pi \) character of the formal CC single bonds is 15% on the average while that of the formal double bonds is about 84%. Complete peripheral delocalization would yield a \( \pi \) character of 50% and a RE higher than that of benzene (21 kcal/mol13) but lower than that of naphthalene (30.3 kcal/mol13). Hence the calculated extent of electron delocalization suggests that 1 is slightly stabilized, its RE being probably lower than 7 kcal/mol.

In order to assess the RE of 1 directly, we have calculated the homodesmic reaction enthalpy (HRE)11 of 1 at the MNDOC level of theory. The HRE value of 1 contains both the RE of the 10π system and the strain energies (SE) of the four- and eight-membered ring. The latter can be approximated by those of 3,4-dimethylene-cyclobutene (11) and planar \( D_{6h} \) cyclooctatetraene (12). In order to eliminate strain effects, the homodesmic reactions of 11 and 12 are subtracted from that of 1, thus yielding the formal reaction 1. The reaction enthalpy

\[ \Delta H_F \text{ of 1 is calculated to be 6.9 kcal/mol. This value comprises the REs of 11, and 12. While 11 is generally considered to be nonaromatic (RE = 0 \pm 1 kcal/mol15,16), 12 is slightly antiaromatic possessing a RE of -2.5 \pm 0.5 kcal/mol.17 Utilizing this value we get a RE of 4.4 \pm 1.5 kcal/mol for 1, i.e., 1 is slightly stabilized by partial \( \pi \)-electron delocalization along the periphery of the bicyclic carbon framework. Accordingly, one can consider 1 to be weakly aromatic. This result supports Oda's description of 1 but contradicts the MMP2 RE value of -4 kcal/mol, which is outside the error margin of our calculation. We attribute this discrepancy to the MMP2 description of the four-membered ring of (Table I), in particular the 1,8-bond length, which comes out far too short at the MMP2 level (see point 3, above). Hence, the cyclobutadiene character of the four-membered ring is artificially increased leading to the calculated overall destabilization of 1 at the MMP2 level.6 Vogel and co-workers have shown that 1 can be generated from its \( \eta^4 \)-tricarbonyliron complex (8, Scheme I) by oxidation with \( \text{CH}_3\text{NO}_2 \).5 The oxidation process may directly lead to 1 (path A in Scheme I) as is generally assumed in the case of \( \eta^4 \)-complexes of cyclobutadiene.11a On the other hand, the possibility of a stepwise decomplexation process into an \( \eta^2 \)-intermediate or transition-state (TS) structure (paths B and C in Scheme I) cannot be fully excluded. For example, \( \eta^2 \)-iron complexes have been observed for 11 and benzocyclobutadiene. In addition, they are likely intermediates in the isomerization of \( \eta^4 \)-diene-tricarbonyliron complexes.15

If complexes 9 and/or 10 are formed, oxidation will lead to the valence tautomeric forms 2 and 3, which may also be intermediates of the process 8 \( \rightarrow \) 4 \( \rightarrow \) 1 (Scheme I). According to the \( \pi \) interaction diagram shown in Figure 3, 2 should be more stable than 3. For 2, there are stabilizing two-electron interactions between the frontier orbitals of the cyclobutadiene and the hexatriene unit while for 3 a destabilizing four-electron interaction is encountered.

ticated. Since stabilizing and destabilizing interactions are largest in the planar forms, 3 should adopt the tub form while 2 should be planar. The predictions are confirmed by MNDOC calculations. All attempts of detecting a nonplanar form for 2 failed. In principle, 2 already possesses the possibility of delocalizing its π electrons along the periphery of the bicyclic system, thus getting rid of high cyclobutadiene character, which causes an antiaromatic destabilization of 2. The RE of 2 can be derived from that of 1 by considering that both 2 and 1 are (almost) planar and possess both similar SEs. Hence, the RE value of 2 is $\Delta H_f^\circ(2) = \Delta H_f^\circ(1) + \Delta H_f^\circ(2) - \Delta H_f^\circ(1) = -7 \text{ kcal/mol}$. Although 2 is still aromatic, its RE value suggests that the cyclobutadiene character of the four-membered ring is considerably reduced due to significant lengthening of the 1,5-bond ($R = 1.560 \text{ Å}$; MNDOC) and partial delocalization of the 4π system into the eight-membered ring ($R(1,10) = 1.367$; $R(9,10) = 1.482 \text{ Å}$).

Decomplexation of 10 yields 3, which contains a 1,8-double bond. Accordingly, substantial delocalization of 10π electrons along the periphery of the bicyclic system is no longer possible. As predicted from consideration of π MOs (Figure 3) 3 is puckered with folding angles $\alpha$ and $\beta$ (25°, 32°) similar to those of 12 (experimental, 44°20, MNDOC, 39). In this way, both strain and unfavorable π electron interactions in the eight-membered ring are reduced. According to theory, 3 is 23 kcal/mol less stable than 1, a value, which can be rationalized as arising from the loss of the RE of 1 (4 kcal/mol) and a destabilization of 3 by the RE of the antiaromatic cyclobutadiene unit (−19 kcal/mol18,17). This explanation implies, however, that opposing changes in the SEs cancel each other out.

Valence tautomerization from 2 or 3 to 1 implies a bond shift along the periphery of 2 (path B) or a bond shift in the planar eight-membered ring of 3 (path C). Hence, forms 5 and 6 should resemble the TS of path B (TSB) and C (TSC), respectively. According to theory 5 is more stable than 2 and 6 more stable than 3 (Scheme I). This is due to the fact that neither 5 nor 6 any longer contain the highly destabilized cyclobutadiene entity. It turns out to be rather difficult to establish reaction coordinates leading from 2 and 3 to 1. A continuous change of the bond lengths of either the four-membered ring (2) or the eight-membered ring (2, 3) to the corresponding values calculated for 1 leads to a continuous increase of the energy by 5–6 kcal/mol followed by a sudden drop of the energy to the value of 1. This is indicative of an improper choice of the reaction coordinate. In addition, there is an orbital crossing of HOMO and LUMO if 3 (for frontier orbital symmetries see Figure 3) rearranges to C, symmetrical 1 (symmetries of HOMO and LUMO are A and S). Although this becomes partially allowed due to the weakly broken symmetry of 1, it adds to the difficulties of establishing the reaction coordinate of path C. Assuming that ring flattening will precede a bond shift in 3, an energy increase of 2 kcal/mol is calculated which can be considered as the lower bound of the barrier of path C (TSC). Similarly, the energy of 6 can be used by deriving a lower bound of 2.3 kcal/mol for path B (TSB). Hence, the actual barrier values will lie between 2 and 5 kcal/mol which means that an experimental observation of either 2 or 3 is hardly possible under conditions of an oxidation of 8.3

This holds also for 4 which can rearrange without any barrier directly to 1, thereby possibly traversing form 7 (Scheme I).

Inspection of the calculated $\Delta H_f^\circ$ values of 5 and 6 reveals that the degenerate valence tautomerization of 1 proceeds via a totally delocalized 10π system ($R = 1.394 \text{ Å}$) with a long 1,8-bond ($R = 1.549 \text{ Å}$). The corresponding barrier value is only 3.8 kcal/mol. Bond shifting in the eight-membered ring of 1 requires 13.6 kcal/mol which is somewhat lower than the corresponding barriers observed for substituted cyclooctatetraenes (14–16 kcal/mol17).

Although neither 2 nor 3 are likely to be observed experimentally, it might be possible to stabilize at least one of them by benzannelation.22 We have investigated this possibility by calculating geometries and heats of formation of 14, 15, and 16 (Figure 4, Table III). It turns out that 14, which corresponds to 1, is less stable than both 15 and 16 by 5.4 and 3 kcal/mol. Obviously, a peripheral delocalization of 14π electrons in 14 is energetically less favorable than preservation of the 6π system of benzene although the latter irrevocably leads to a cyclobutadiene unit (15 and 16). The synthesis of 15 (or the corresponding dibenzo and tribenzo derivatives of 2) appears as an interesting experimental goal on the basis of our calculations. It would provide evidence on the electronic features of a conjugated hydrocarbon containing both an aromatic and antiaromatic π system.

Conclusions

Our investigation leads to the following conclusions. (1) Bicyclo[6.2.0]decapentaene (1) is weakly aromatic possessing a RE of 4 kcal/mol. (2) Its valence tautomer forms 2 and 3 are less stable by 11 and 23 kcal/mol due to their inherent antiaromatic character. (3) If formed during the oxidation of the $\eta^4$-tricarbonyliron complex of 1, neither 2 nor 3 should be experimentally detectable due to their low kinetic (and thermodynamical) stability. (4) Benzannelation of bicyclo[6.2.0]decapentaene at bond 4,5 stabilizes both form 2 and 3 and provides a possibility of

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(19) These attempts were mainly of theoretical interest: a nonplanar form of 2, although unlikely in view of favorable π-electron delocalization in planar 2, has been calculated by Allinger et al.6 Again, this seems to be an artifact of the MMP2 description.

investigating a $r$-system (15) containing the cyclobutadiene ring.

Acknowledgment. We thank Prof. E. Vogel for suggesting this work. Support by the Deutsche Forschungsgemeinschaft and the Rechenzentrum der Universität Köln is gratefully acknowledged. T.S. thanks the Stipendienfonds des Verbandes der Chemischen Industrie for a generous grant.

Registry No. 1, 20455-01-0.

Supplementary Material Available: Tables II and III containing calculated $\Delta H^\circ$ values and geometries (6 pages). Ordering information is given on any current masthead page.

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Metal Catalysis in Oxidation by Peroxides.\(^1\) Sulfide Oxidation and Olefin Epoxidation by Dilute Hydrogen Peroxide Catalyzed by Molybdenum and Tungsten Derivatives under Phase-Transfer Conditions

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35131 Padova, Italy

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A procedure is described which allows the oxidation of nucleophilic substrates such as organic sulfides or alkenes, under phase-transfer conditions, by employing dilute hydrogen peroxide, Mo(VI) and W(VI) catalysts, and a neutral lipophilic monodentate ligand as extracting agent. The yields and selectivities observed are generally rather high, thus establishing the synthetic relevance of the method. The success of this procedure, and particularly the efficiency of monodentate ligands, is also discussed from a mechanistic point of view.

Table I. Monodentate Neutral Ligands

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<td>CH$_2$(CH$_2$)$_11$</td>
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<td>TDPT</td>
<td></td>
</tr>
</tbody>
</table>

the ligand $L$ is strongly bound to the metal.\(^7\) The dehydrated complexes $\text{MO(O}_2)\text{L}$ are soluble in many organic solvents and have been used as effective stoichiometric oxidants of several nucleophilic substrates.\(^8\)

There is now evidence that the displacement of the neutral ligand $L$ by the substrate is not a prerequisite for the occurrence of the oxygen-transfer process.\(^9,10\) On the other hand, $L$ is continuously released in the reaction medium with the progress of the oxidation, owing to the low affinity of such ligands for the reduced oxo species of Mo(VI) and W(VI).\(^5\)

These observations convinced us of the feasibility of an oxidizing procedure based on a two-phase system.\(^10\) In such a system, the neutral Mo(VI) or W(VI) peroxo complexes formed in aqueous solution are extracted by a lipophilic, monodentate, neutral ligand in an organic phase, usually dichloroethane, where the oxidation of the substrate takes place.

The experimental results reported in this paper illustrate in a quantitative way the features which make the procedure synthetically valuable. Among these, an obvious...