mass spectrum, m/e (relative intensity) 187 (5), 171 (5), 173 (5), 163 (10), 162 (100), 132 (8), 76 (7), 58 (10). Anal. Calcd for $C_{15}H_{21}NO_3$: C, 68.41; H, 8.04; N, 5.32. Found: C, 68.22; H, 7.80; N, 5.66. The other diastereoisomer of 4e, mp 154–155 °C; showed: IR (CHCl$_3$) 3360, 1700 cm^{-1}; NMR (CDCl$_3$) δ 0.50 (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), 163 (13), 162 (100), 133 (6), 70 (5), 59 (10), 55 (13). Anal. Calcd for $C_{15}H_{21}NO_3$: C, 68.41; H, 8.04; N, 5.32. Found: C, 68.53; H, 8.36; N, 5.15.

2,3-Dimethyl-2-butene. Workup gave 53 mg (26%) of NMP and 100 mg (42%) of 6, mp 105–106 °C, along with two isomeric photoreduction products (eq 2). Compound 6 showed: IR (CHCl$_3$) 3460, 1688, 1672 cm^{-1}; NMR (CDCl$_3$) δ 1.26 (s, 6 H), 1.28 (s, 6 H), 2.87 (d, J = 5 Hz, 3 H), 3.28 (s, 3 H), 6.00–6.50 (b s, 1 H), 7.00–7.80

(m, 4 H); mass spectrum, m/e (relative intensity) 173 (7), 163 (13), 162 (100), 85 (13), 74 (27), 72 (7), 69 (8). Anal. Calcd for $C_{16}H_{23}NO_2$: C, 69.31; H, 8.30; N, 5.05. Found: C, 68.97; H, 8.21; N, 5.27.

Theoretical Determination of Molecular Structure and Conformation. 14. Is Bicyclo[6.2.0]decapentaene Aromatic or Antiaromatic?

Dieter Cremer* and Thomas Schmidt

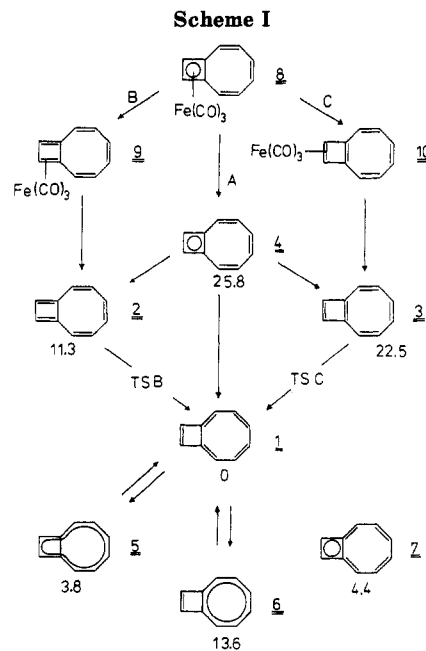*Institut für Organische Chemie, Universität Köln, D-5000 Köln 41, West Germany*

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Ab initio HF/STO-3G and MNDOC calculations on bicyclo[6.2.0]decapentaene (1) suggest that 1 possesses a slightly puckered equilibrium structure with C_1 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[1] and theoreticians,[2,3] in particular after the first successful synthesis of the parent compound (1, see Scheme I) by Oda and co-workers.[4,5] 1 contains in its periphery $(4n + 2)$ 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

Scheme I

of the antiaromatic character of the component rings of 1.[2] These predictions have recently been supported by results of an elaborate MMP2 force field investigation of 1 carried out by Allinger and Yuh.[6] By making an as-

(1) For the synthesis of derivatives of 1, see: (a) Magon, M.; Schröder, G. *Liebigs Ann. Chem.* **1978**, 1379–1389. (b) Oda, M.; Oikawa, H.; Fukazawa, N.; Kitahara, Y. *Tetrahedron Lett.* **1977**, 4409–4412. (c) Kaplan, F. A.; Roberts, B. W. *J. Am. Chem. Soc.* **1977**, *99*, 513–517, 518–522. (d) Schröder, G.; Ramadas, S. R.; Nikoloff, P. *Chem. Ber.* **1972**, *105*, 1072–1083. (e) Schröder, G.; Martini, T. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 806–807.

(2) (a) Aihara, J. *J. Am. Chem. Soc.* **1981**, *103*, 5704–5706. (b) Gastmans, J. P.; Gastmans, D. F.; Slade, S. F. *Can. J. Chem.* **1979**, *57*, 2864–2868. (c) Randic, M. *J. Am. Chem. Soc.* **1977**, *99*, 444–450. See also: (d) Dewar, M. J. S. *Tetrahedron* **1966**, *22*, 75–92. (e) Rosowsky, A.; Fleisher, H.; Young, S. T.; Partch, R.; Saunders, W. H., Jr.; Boekelheide, V. *Tetrahedron* **1960**, *11*, 121–124.

(3) For NDO calculations on 1 see: (a) Mak, T. C. W.; Li, W. K. *J. Mol. Struct.* **1982**, *89*, 281–284. (b) Tajiri, A.; Hatano, M.; Oda, M. *Chem. Phys. Lett.* **1981**, *78*, 112–116. (c) After this investigation had been finished a MNDO study of 1 was published: Glidewell, C.; Lloyd, D. *Tetrahedron* **1984**, *40*, 4455–4472.

(4) Oda, M.; Oikawa, H. *Tetrahedron Lett.* **1980**, *21*, 107–110.

(5) For an alternative approach to 1 see: Kawka, D.; Mues, P.; Vogel, E. *Angew. Chem.* **1983**, 1006–1007; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 1003–1004.

(6) Allinger, N. L.; Yuh, Y. H. *Pure Appl. Chem.* **1983**, *55*, 191–197.
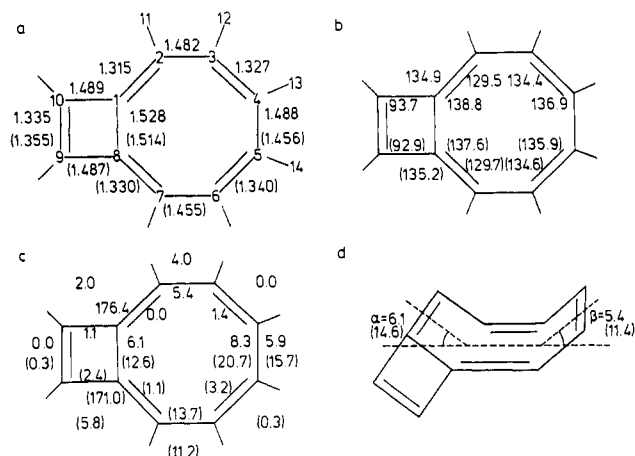
Figure 1. Ab initio (HF/STO-3G) and MNDOC (in parentheses) structural parameters of C_1 symmetrical 1. Since parameters, which would be related by symmetry in the C_s form of 1, possess similar values, only their average is given. (a) Bond lengths (Å). (b) Bond angles. (c) Absolute values of dihedral angles. (d) Folding angles α and β (deg). Computed CCCC dihedral angles are shown inside, HCCH angles outside the two rings at the CC bond in question. The value of 176.4° (171.0°) corresponds to dihedral angle 10, 1, 2, 3.

sessment of the conflicting influences of π delocalization and ring strain, these authors calculated a resonance energy (RE) of -4 kcal/mol for 1, a value, which is typical for an antiaromatic $4n$ π system. This, however, contradicts experimental evidence gathered by Oda and co-workers which lends support to the characterization of 1 as an (weakly) aromatic 10π electron system.[7]

We now wish to report on the electronic structure of 1 as obtained by ab initio calculations (HF/STO-3G[8]) and complemented by extensive MNDO and MNDOC[9] calculations both on 1 and the related forms 2-7 (see Scheme I). Our investigation is aimed at solving the contradiction 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 $\rho(r)$ of 1. Special emphasis is laid on an appropriate analysis of the latter in order to obtain CC bond orders n and bond ellipticities ϵ.[10] As has been recently shown both quantities allow a description of the degree of π electron delocalization in a conjugated system.[11]

Computational Details. Employing gradient and quasi-Newton methods with an analytical determination of energy derivatives, complete geometry optimizations of forms 1-7 have been carried out within the following symmetrical and geometrical constraints. 1: C_1 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: C_s symmetry; the

(7) Kabuto, C.; Oda, M. *Tetrahedron Lett.* **1980**, *21*, 103-106.

(8) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657-2664.

(9) (a) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899-4907. (b) Thiel, W. *J. Am. Chem. Soc.* **1981**, *103*, 1413-1420, 1420-1425. (c) The energetic effect of quadruple excitations has been determined by formulas suggested: Langhoff, S. R.; Davidson, E. R. *Int. J. Quantum Chem.* **1974**, *8*, 61-65. Pople, J. A.; Seeger, R.; Krishnan, R. *Int. Quantum Chem. Symp.* **1977**, *11*, 149-163.

(10) Bader, R. F. W.; Slee, T. S.; Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1983**, *105*, 5061-5068.

(11) (a) Cremer, D.; Kraka, E.; Slee, T. S.; Bader, R. F. W.; Lau, C. D. H.; Nguyen-Dang, T. T.; Mac Dougall, P. J. *J. Am. Chem. Soc.* **1983**, *105*, 5069-5075. (b) Cremer, D.; Kraka, E. *Croat. Chem. Acta* **1984**, *57*, 1265-1281. (c) Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1985**, *107*, 3811-3819.

Table I. Comparison of Theoretical and Experimental Structural Data of 1 and *trans*-1,3-Butadiene[a]

parameter	HF/STO-3G	expt[b]	MNDOC	MNDO	MMP2[c]
R(1,2)	1.315	1.336	1.330	1.341	1.342
R(2,3)	1.482	1.432	1.455	1.460	1.455
R(3,4)	1.327	1.374	1.340	1.350	1.354
R(4,5)	1.488	1.415	1.456	1.461	1.462
R(1,8)	1.528	1.535	1.514	1.505	1.475
R(1,10)	1.489	1.446	1.487	1.491	1.471
R(9,10)	1.335	1.403	1.355	1.367	1.365
		trans-butadiene			
R(1,2)	1.313	1.341[d]	1.329	1.344	1.346[e]
R(2,3)	1.488	1.463[d]	1.465	1.465	1.471[e]

[a] Bond lengths in Å. [b] 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. [c] Force field calculations from ref 6. [d] Almenningen, A.; Bastiansen, O.; Traetteberg, M. *Acta Chem. Scand.* **1958**, *12*, 1221. [e] Kao, J.; Allinger, 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: C_{2v} 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: C_{2v} 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, and 3 are located at minima of the MNDO or the (correlation-corrected) MNDOC[9] energy hypersurface of bicyclo[6.2.0]decapentaene.

Results and Discussions

In Figure 1, averaged bond lengths, averaged bond angles, averaged dihedral angles, and the folding angles α and β of C_1 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., 1 possesses C_1 symmetry rather than C_{2v} or C_s symmetry (see Figure 1 part d). The actual deviation from C_s 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 $\alpha = \beta = 0°$. 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.[7]

(3) The calculated central bond length (C_1–C_8) 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[7]) but contrary to the MMP2 force field result (1.475 Å[6]).

(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 I). MNDO (MNDOC) values are in good agreement with experimental data while ab initio values differ on the average by 0.04 Å. The latter

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 π character of a CC bond (in percent) by the ratio $\eta = 100 \times \epsilon\text{-}(CC)/\epsilon(\text{ethylene})$ where the bond ellipticity ϵ measures the anisotropy of $\rho(r)$ at a CC bond.[10] The value of η is large if the π character of a CC bond is fully established (η-(ethylene) = 100%) while it is zero for a CC bond without any π contributions.

Our results suggest that the 1,8-bond of 1 possesses only low π character ($\eta < 10\%$, see Figure 2). According to calculated bond orders n and bond ellipticities ϵ (π character η), delocalization of π electrons occurs essentially along the periphery of the bicyclic system. The π 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 π character of 50% and a RE higher than that of benzene (21 kcal/mol[13]) but lower than that of naphthalene (30.3 kcal/mol[13]). 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 homodesmotic reaction enthalpy (HRE)[14] 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_{4h} cyclooctatetraene (12). In order to eliminate strain effects, the homodesmotic reactions of 11 and 12 are subtracted from that of 1, thus yielding the formal reaction 1. The reaction enthalpy
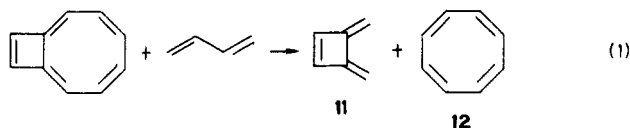
$\Delta\Delta H_f°$ of 1 is calculated to be 6.9 kcal/mol. This value comprises the REs of 1, 11, and 12. While 11 is generally considered to be nonaromatic (RE = 0 ± 1 kcal/mol[15,16]) 12 is slightly antiaromatic possessing a RE of −2.5 ± 0.5 kcal/mol.[17] Utilizing this value we get a RE of 4.4 ± 1.5 kcal/mol for 1, i.e., 1 is slightly stabilized by partial 10π 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 1 (Table I), in particular the 1,8-bond length,

(12) See, for example: Cremer, D.; Dick, B.; Dines, C. *J. Mol. Struct.* (*Theochem.*) **1984**, *110*, 277–291.

(13) (a) George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *Tetrahedron* **1976**, *32*, 1357–1362. (b) George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1222–1227. (c) George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *Theor. Chim. Acta* **1975**, *38*, 121–129.

(14) George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *Tetrahedron* **1976**, *32*, 317–323.

(15) (a) Skancke, A.; Skancke, P. N. *Acta Chem. Scand.* **1968**, *22*, 175–182. (b) Skancke, A. *Acta Chem. Scand.* **1968**, *22*, 3239–3244. See also ref 16.

(16) Kollmar, H. *J. Am. Chem. Soc.* **1979**, *101*, 4832–4840.

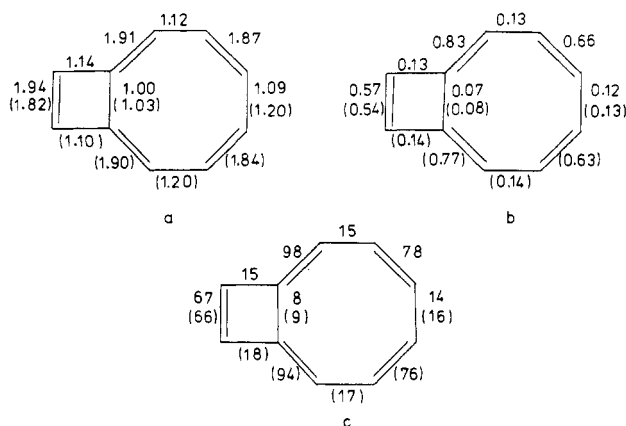(17) Dewar, M. J. S. "The Molecular Orbital Theory of Organic Chemistry"; McGraw-Hill: New York, 1969.

Figure 2. Calculated (HF/STO-3G) bond orders n (a), bond ellipticities ϵ (b), and π character $\eta = 100(\epsilon/\epsilon(\text{ethylene}))$ with $\epsilon(\text{ethylene}) = 0.74$ (c). The latter values are given in percent and are normalized to 500, the π character of five double bonds. Numbers in parentheses correspond to n, ϵ, and η values obtained for the MNDOC geometry.
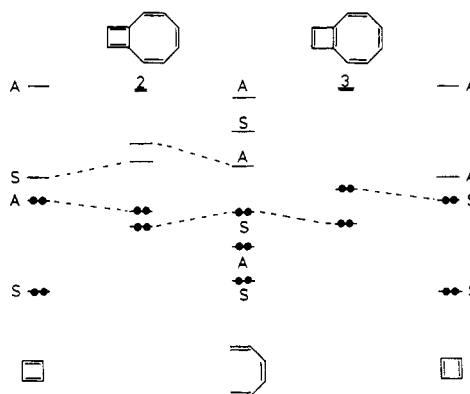

Figure 3. Interactions between the π MOs of the cyclobutadiene and hexatriene moiety of 2 and 3. Only changes of frontier MOs are shown.

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 η^4-tricarbonyliron complex (8, Scheme I) by oxidation with $(CH_3)_3NO$.[5] The oxidation process may directly lead to 1 (path A in Scheme I) as is generally assumed in the case of η^4-complexes of cyclobutadiene (13).[18a] On the other hand, the possibility of a stepwise decomplexation process via an η^2-intermediate or transition-state (TS) structure (paths B and C in Scheme I) cannot be fully excluded. For example, η^2-iron complexes have been observed for 11 and benzocyclobutadiene. In addition, they are likely intermediates in the isomerization of η^4-diene–tricarbonyliron complexes.[18]

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 π 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 encoun-

(18) (a) Deeming, A. J. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Vol. 4, pp 377–512. (b) Kerber, R. In "The Organic Chemistry of Iron"; Koerner von Gustorf, E. A., Grevels, F. W., Fischler, I., Eds.; Academic Press: New York, 1981; Vol. 2, pp 1–153.

tered. 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.[19] 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 RE(**2**) = RE(**1**) $-[\Delta H_f°(2) - \Delta H_f°(1)]$ = -7 kcal/mol. Although **2** is still antiaromatic, its RE value suggests that the cyclobutadiene character of the four-membered ring is considerably reduced due to significant lengthening of the 1,8-bond (R = 1.560 Å; MNDOC) and partial delocalization of the 4π system into the eight-membered ring ($R(1,10)$ = 1.367; $R(9,10)$ = 1.482 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 α and β (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/mol[16,17]). 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_s 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**.[5] This holds also for **4** which can rearrange without any
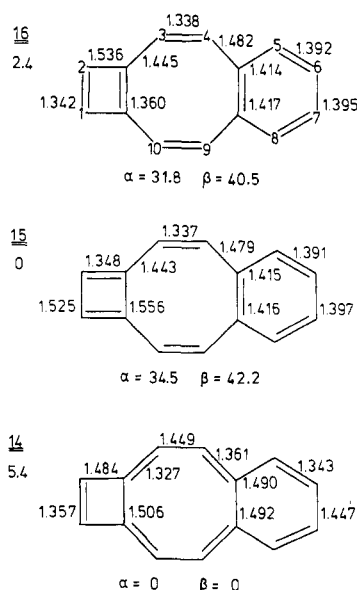

Figure 4. Calculated MNDOC bond lengths (Å), folding angles (deg), and relative enthalpies $\Delta\Delta H_f°$ (kcal/mol) of **14**, **15**, and **16**.

barrier directly to **1**, thereby possibly traversing form **7** (Scheme I).

Inspection of the calculated $\Delta H_f°$ values of **5** and **6** reveals that the degenerate valence tautomerization of **1** proceeds via a totally delocalized 10π system (R = 1.394 Å) with a long 1,8-bond (R = 1.549 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/mol[21]).

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**[23]) 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 tautomeric 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 η^4-tricarbonyliron complex of **1**, neither **2** nor **3** should be experimentally detectable due to their low kinetic (and thermodynamical) stability. (4) Benzoannelation of bicyclo[6.2.0]decapentaene at bond 4,5 stabilizes both form **2** and **3** and provides a possibility of

(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.

(20) Traetteberg, M. *Acta Chem. Scand.* **1966**, *20*, 1724–1726.

(21) Gardlik, J. M.; Paquette, L. A.; Gleiter, R. *J. Am. Chem. Soc.* **1979**, *101*, 1617–1620 and references cited therein.

(22) (a) Berris, B. C.; Vollhardt, K. P. C. *Tetrahedron* **1982**, *38*, 2911–2917. (b) Engels, H.-W. PhD thesis, 1980, Köln.

(23) See, for example: Wong, H. N. C.; Sondheimer, F. *Tetrahedron Lett.* **1976**, 2715–2718.

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

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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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.

The availability of a vast body of information on the chemistry of peroxo metal species has already made possible remarkable achievements in transition metal-catalyzed oxidations by peroxides.[2] Therefore, very efficient and selective, including chemo-, regio-, and enantioselectivity, synthetic procedures, employing either hydrogen peroxide or alkyl hydroperoxides combined with a variety of metal derivatives, have been reported in recent years.[3]

It is well-known that molybdenum(VI) or tungsten(VI) peroxo complexes, in aqueous solution, are readily formed by addition of hydrogen peroxide to H_2MO_4 acids;[4] the resulting peroxo species are also fairly acidic so that they are largely present as anions in solutions.[4,5] However, by adjusting the acidity of the medium, neutral peroxo compounds may be obtained[6] which, upon addition of an appropriate neutral ligand L (HMPT, DMF, PyO, etc.), precipitate as the sparingly water soluble complexes MO-$(O_2)_2L,H_2O$. In these species, the water molecule is only weakly coordinated and may be easily removed whereas

Table I. Monodentate Neutral Ligands

	R	R′	abbreviation
$[RR'N]_3P{=}O$	CH_3	CH_3	HMPT
	CH_3CH_2	CH_3CH_2	HEPT
	$CH_3(CH_2)_3$	$CH_3(CH_2)_3$	HBPT
	cyclohexyl	H	TCyPT
	$CH_3(CH_2)_{11}$	H	TDPT
4-R-pyridine *N*-oxide	$Ph(CH_2)_3$		RPyNO
	$CH_3(CH_2)_8$		R′PyNO

the ligand L is strongly bound to the metal.[7] The dehydrated complexes $MO(O_2)_2L$ are soluble in many organic solvents and have been used as effective stoichiometric oxidants of several nucleophilic substrates.[6,8]

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.[2b,3a,9] 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).[6]

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

(1) Metal Catalysis in Oxidation by Peroxides. Part 21. Part 20: Bortolini, O.; Conte, V.; Di Furia, F.; Modena, G. *Nouv. J. Chim.* **1985,** *9,* 147.

(2) (a) Sheldon, R. A.; Kochi, J. K. "Metal-Catalyzed Oxidations of Organic Compounds"; Academic Press: New York, 1981. (b) Di Furia, F.; Modena, G. *Pure Appl. Chem.* **1982,** *54,* 1853. (c) Mimoun, H. "The Chemistry of Functional Groups, Peroxides"; Patai, S., Ed.,; Wiley: New York, 1982, pp. 463–482. (d) Sheldon, R. A. *Ibid.* pp 161–200.

(3) (a) Sharpless, K. B.; Verhoeven, T. R. *Aldrichimica Acta* **1979,** *12,* 63. (b) Pralus, M.; Lecoq, J. C.; Schirmann, J. P. "Fundamental Research in Homogeneous Catalysis"; Tsutsui, M., Ed.; Plenum Press: New York, 1979, Vol. 3, pp 327–343. (c) Mimoun, H.; Saussine, L.; Daire, E.; Postel, M.; Fischer, J.; Weiss, R. *J. Am. Chem. Soc.* **1983,** *105,* 3101. (d) Mimoun, H. *Pure Appl. Chem.* **1981,** *53,* 2389. (e) Venturello, C.; Alneri, E.; Ricci, M. *J. Org. Chem.* **1983,** *48,* 3831.

(4) Connor, J. A.; Ebsworth, E. A. V. *Adv. Inorg. Chem. Radiochem.* **1964,** *6,* 279.

(5) (a) Arcoria, A.; Ballistreri, F. P.; Tomaselli, G. A.; Di Furia, F.; Modena, G. *J. Mol. Catal.* **1983,** *18,* 177. (b) Arcoria, A.; Ballistreri, F. P.; Tomaselli, G. A.; Di Furia, F.; Modena, G. *Ibid.* **1984,** *24,* 189. (c) Raciszewski, Z. *J. Am. Chem. Soc.* **1960,** *82,* 1267.

(6) Mimoun, H.; Sérée de Roch, I.; Sajus, L. *Bul. Soc. Chim. Fr.* **1969,** 1481; *Tetrahedron* **1970,** *26,* 37.

(7) Le Carpentier, J. M.; Mitschler, A.; Weiss, R. *Acta Crystallogr. Sect. B.* **1972,** *B28,* 1288.

(8) Arakawa, H.; Moro-Oka, Y.; Nozaki, A. *Bull. Chem. Soc. Jpn.* **1974,** *47,* 2958.

(9) Di Furia, F.; Modena, G. *Rev. Chem. Intermed.* **1985,** *6,* 51.

(10) Bortolini, O., Di Furia, F., Modena, G. Italian Patent Applications 25720A and 25721A, 1981.