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# 161. Cyclooct-1-en-5-yne. Preparation, Spectroscopic Characteristics and Chemical Reactivity[1])

by **Werner Leupin** and **Jakob Wirz**

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(22.III.78)

## *Summary*

Cyclooct-1-en-5-yne (**3**) has been obtained as an isolable, but highly reactive hydrocarbon by oxidation of cyclooct-5-ene-1,2-dihydrazone with lead tetraacetate *(Scheme 2)*. Information regarding the structure and conformational mobility of **3** has been gained from the analysis of its $^1$H- and $^{13}$C-NMR. spectra and was found to agree with the results of force field calculations. Photolysis (206 nm) of **3** in solution has induced cleavage to butatriene and butadiene. The first band in the photoelectron spectrum of **3** ($I_v$ 9.10 eV) is attributed to ionization from a rather delocalized orbital with predominant weight of the double bond p-AO's. Nevertheless, the high reactivity of **3** stems from the strained triple bond as evidenced by the reaction products obtained by pyrolysis, oxidation, *Diels-Alder* addition, and 1,3-dipolar addition *(Scheme 4)*.

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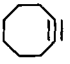
[1]) Presented at the Swiss Chemical Society meeting, 7.10.1977.

**Introduction.** - The incorporation of unsaturation in hydrocarbon structures is generally associated with increased rigidity due to the loss of rotational degrees of freedom and to the increased strength of the multiple bonds. Notwithstanding, the triple bond is the most flexible structural subunit in hydrocarbons with respect to distortions from equilibrium bond angles. The ease with which a deformation of the C–C≡C system takes place is demonstrated by the fact that cyclic acetylenes down to cyclopentyne [1] and norbornyne [2] can be generated by hydrohalide elimination from the corresponding vinyl halide, though the high reactivity of the lower members has prevented their isolation. The smallest unsubstituted cycloalkynes yet isolated are cyclooctyne (**1**) [3] and 1,5-cyclooctadiyne (**2**) [4] both of which exhibit a deviation of the C≡C–C angles from linearity of 21°.

Cyclooct-1-en-5-yne (**3**) has hitherto only been reported to exist as a ligand in a ruthenium cluster complex formed by reaction of 1,5-cyclooctadiene with $\alpha$-$H_4Ru(CO)_{12}$; the structure of the complex has been determined by X-ray analysis but according to the authors 'the conformation of the macrocyclic ligand is obviously dictated by the bonding and steric requirements of the cluster' [5]. From a qualitative consideration of the geometric constraints imposed on the free hydrocarbon **3**, we expected that it should adopt a rather rigid nonplanar conformation and that the *cis*-bending of the acetylenic moiety should be somewhat larger than in **1** and **2**. In keeping with the latter prediction, the following observations suggested that **3** should be more reactive than both **1** or **2**: (*i*) *Diels-Alder* addition of **2** to butadiene has yielded only the bis-adduct even when an excess of **2** was allowed to react with the diene [4] *(Scheme 1)*; (*ii*) the benzo-derivative **4** has been reported to be too unstable for isolation [6a] (note also the high reactivity of isomer **5** [6b]), and (*iii*) in the dibenzo-series **6** to **8** [7], **7** is distinctly more reactive than **6** or **8**. Compound **9**, a tetramethyl derivative of **4**, has recently been synthesized by *Krebs et al.* [6a] and was found to be thermally stable due to the shielding effect of the two *gem*-methyl groups. We now report the synthesis of **3** which appears to be the most highly strained unsubstituted cycloalkyne yet isolated as a pure compound [8].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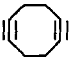
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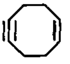
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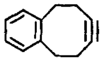
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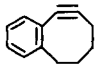
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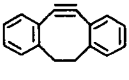
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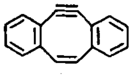
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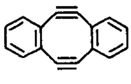
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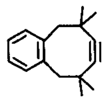
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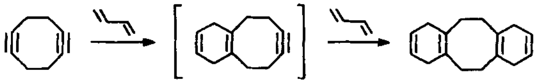
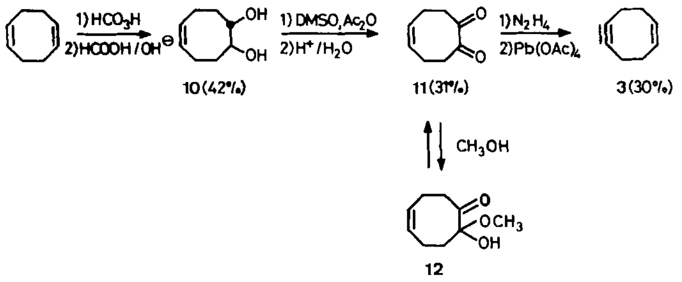
Scheme 1



**Results and Discussion.** - 1. *Preparation and general properties.* Cyclooct-1-en-5-yne (**3**) was synthesized from cyclooct-5-ene-1,2-dione (**11**) [9] by oxidative degradation of its dihydrazone under exclusion of air *(Scheme 2)*. Care should be taken to avoid the conversion of **11** to its hemiacetal **12** in alcoholic solvents.

*Scheme 2*



The hydrocarbon **3** is a colourless, volatile liquid (m.p. $-10°$) of disagreeable odour. It may be stored for a period of months at $-15°$ in an evacuated tube. The structure of **3** is secured by the spectroscopic data given below as well as by the reaction products with various substrates *(Scheme 4)*.

2. *NMR. spectroscopic data.* Apart from providing unequivocal evidence for the molecular constitution assigned to **3**, the proton and $^{13}$C-NMR. spectra yield qualitative but quite detailed insight into the more subtle structural features of this strained hydrocarbon. The 100-MHz-$^1$H-NMR. spectrum of **3** in CDCl$_3$ at ambient temperature exhibits the symmetric multiplet shown in *Figure 1* (2 H, centered at 5.88 ppm) and two complex multiplets (4 H each, in the ranges of 2.6±0.1 and 2.2±0.1 ppm). The 11-line signal in the olefinic region collapses to a singlet when the allylic protons absorbing at 2.6 ppm are decoupled by double irradiation; it was analysed as the $XX'$ part of an $A_2XX'A_2'$ system with the aid of a *Laocoon II* computer program by neglecting the long-range coupling constant $^5J_{AA'}$ and reproduced

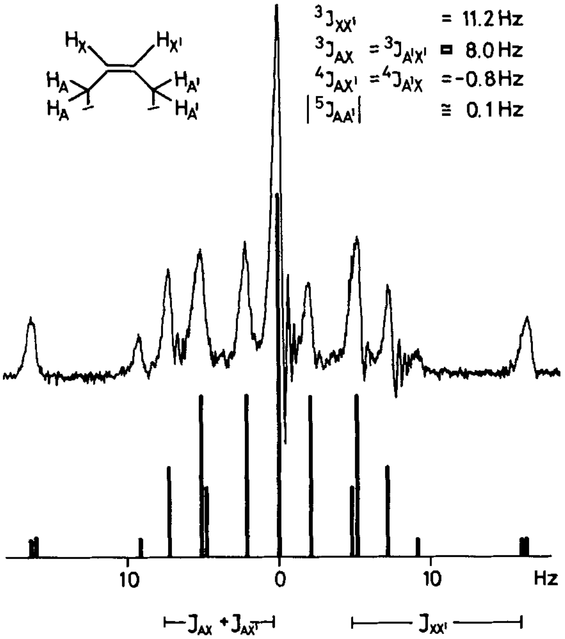
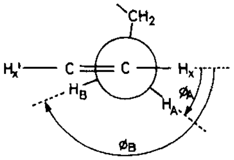


Fig. 1. *Experimental and calculated $^1$H-NMR. spectrum of the olefinic hydrogen atoms of* **3** *centered at* $\delta$ *5.88 ppm*

within experimental accuracy (rms error 0.1 Hz) by iterative least squares fitting. Inclusion of small values for $^5J_{AA'}$ in the calculation resulted in a splitting of most of the lines into closely spaced multiplets while the central line and the lines at $5.88 \pm 0.07$ ppm remained (almost) unaffected. In the experimental spectrum the former lines indeed appear to be slightly broadened which allows us to give an order of magnitude estimate for $^5J_{AA'}$. The analysis yields only the relative signs of the coupling constants. The absolute signs given in *Figure 1* are based on a computer simulation in which the vicinal olefinic coupling constant $^3J_{XX'}$ was assumed positive in accord with current acceptance [10].

The identification of the olefinic protons as the $X$-part of an $A_2XX'A_2'$-system is compatible with either a fully planar equilibrium structure of the carbocycle **3** or the presence of an equilibrium between two equivalent nonplanar conformers, each corresponding to an $ABXX'A'B'$-system, which are rapidly interchanged on the NMR. time scale. In both cases the two protons on each of the allylic methylene groups become magnetically equivalent. The first possibility appears most unlikely on the basis of strain energy considerations and can safely be dismissed by means of a comparison between the observed coupling constants $^3J_{AX}$ and $^4J_{AX'}$ and those predicted by the semiempirical equations (1) derived by *Garbisch* [11]. The dependence of vinyl-allylic coupling constants on the dihedral angle $\phi$ is given by:



$$^3J_{AX} = \begin{cases} 6.6\cos^2\phi + 2.6\sin^2\phi & (\;0° \le \phi \le \;\,90°) \\ 11.6\cos^2\phi + 2.6\sin^2\phi & (90° \le \phi \le 180°) \end{cases}$$

$$^4J_{AX'} = \begin{cases} 1.3\cos^2\phi - 2.6\sin^2\phi & (\;0° \le \phi \le \;\,90°) \\ -2.6\sin^2\phi & (90° \le \phi \le 180°) \end{cases} \tag{1}$$

In the case of rapid exchange between two nonequivalent positions $A$ and $B$ of equal probability the observed coupling constants are equal to the arithmetic mean $\bar{J}$ of the respective values in the two positions. The values $^3\bar{J}_{(AB)X} = 7.7$ and $^4\bar{J}_{(AB)X'} = -0.7$ Hz thus predicted by equation (1) for dihedral angles $\phi_A = 55°$ and $\phi_B = 175°$ ($\phi_B - \phi_A$ assumed 120°) are in good agreement with experiment, whereas the values $^3\bar{J}_{(AB)X} = 3.6$ and $^4\bar{J}_{(AB)X'} = -1.6$ Hz obtained for planar **3** (*i.e.* $-\phi_A = \phi_B = 60°$) are significantly different.

Direct evidence for the postulated dynamic equilibrium comes from the observation of a distinct broadening of the multiplet at 2.6 ppm at temperatures below −30° *(Fig. 2)*. Similar temperature dependent spectra have been previously observed in a number of related cycloalkenes [12]. The high-temperature onset of the coalescence phenomenon in the allylic methylene protons is due to the relatively strong dependence of their chemical shift on the dihedral angle with the olefinic moiety. We have not attempted to obtain the NMR. spectrum in the slow exchange limit, since the presumed complexity of the spectrum even in double resonance experiments would preclude an accurate determination of the involved activation energy by quantitative line-shape analysis. A crude estimate of the inversion barrier separating the two equivalent conformations has nevertheless been obtained by making use of the approximation (2) [10] which is valid, if the coupling constants affecting the allylic protons *A* and *B* are small compared with the chemical shift difference $\Delta\delta = |\delta_A - \delta_B|$.

$$\Delta G^{\neq}(T_c) = 19.1 \cdot T_c \cdot (9.97 + \log T_c - \log \Delta\delta)\ \mathrm{J/mol} \qquad (2)$$

The chemical shift difference $\Delta\delta = 100$ Hz was estimated from the line width at the coalescence temperature $T_c \cong -60°$ *(Fig. 2)*. Similar $\Delta\delta$ values have been accurately determined for related compounds [12]. The free energy of activation $\Delta G^{\neq}(210\ \mathrm{K}) \cong 42$ kJ/mol so obtained must be considered as highly approximate, if compared with the precision achieved in related cases by proper line-shape analysis, but still provides a useful order-of-magnitude estimate. The activation energy for ring inversion in the benzoannelated tetramethyl derivative **9** amounts to $\Delta G^{\neq}(319\ \mathrm{K}) = 70$ kJ/mol [6a].

A final point worth noting in the $^1$H-NMR. spectrum of **3** is the large value of the olefinic coupling constant $^3J_{XX'}$. The bond angle dependence of vicinal coupling constants in cycloalkenes has been noted by several authors and has been quantified by *Cooper & Manatt* [13] in a critical reevaluation of the available data. Their empirical relationship corresponds closely to the dependence predicted by *Karplus* [14] on the basis of valence bond calculations. By insertion of our value $^3J_{XX'} = 11.2$ Hz into the graphical representation given in [13] we predict a value of 126° for the C=C–C bond angles in **3**.

Four signals are observed in the $^1$H spin-decoupled $^{13}$C-NMR. 25.2-MHz-spectrum of **3** in $CDCl_3$ at $\delta_{TMS}$ 131.4, 100.4, 30.8, and 19.2 ppm which may be

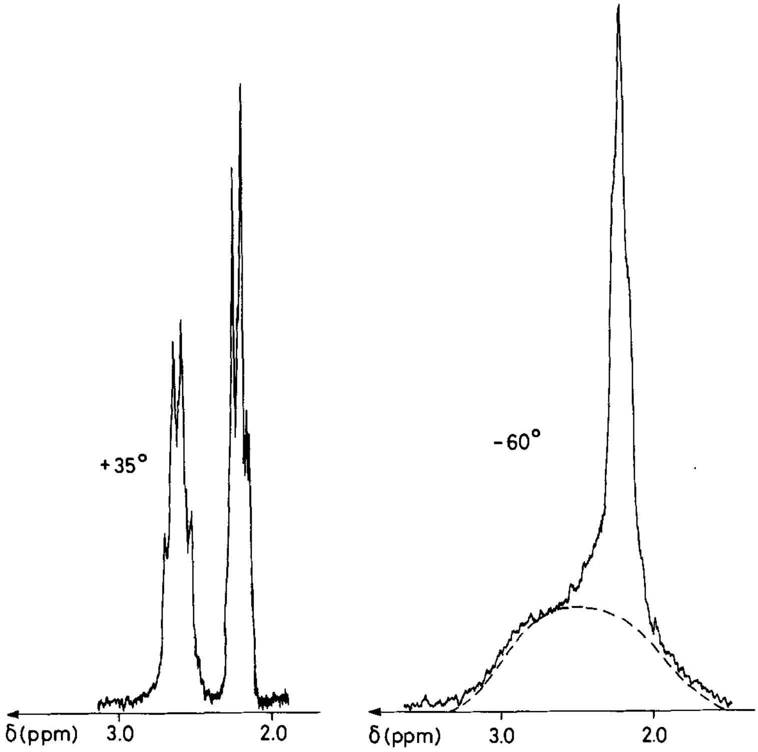


Fig. 2. *T-Dependence in the $^1$H-NMR. spectrum of the allylic hydrogen atoms of* **3** *centered at δ 2.6 ppm*

attributed to the carbon atoms C(1,2), C(5,6), C(3,8), and C(4,7), respectively. The assignment of the former two signals is proven by the splitting patterns in the undecoupled spectrum, C(1,2) (*d*, *J* 152 Hz) and C(5,6) (*s*), while the assignment of C(3,8) (*t*, *J* 128 Hz) and C(4,7) (*t*, *J* 135 Hz) rests on the comparison of their chemical shifts with reference compounds such as **2** and 1,5-cyclooctadiene. The unusually small coupling constant $^1J_{CH}$ 152 Hz at the olefinic carbon atoms again points to a larger-than-average C=C–C bond angle [13]. A correlation between $^{13}C$ chemical shifts of acetylenic carbon atoms and the deviation $\Delta\alpha$ from linearity of the C≡C–C bond angles in strained cycloalkynes was noted by *Krebs & Kimling* [15]. By comparison with their data and those of **2** ($\Delta\alpha$ 21°, $\delta$(–C≡) 95.8 ppm [4]) we estimate $\Delta\alpha$ (**3**) as 25 to 30° on the basis of the observed shift of $\delta$(–C≡) 100.4 ppm. The $^{13}C$-spectra are compatible with the postulated rapid equilibration between two equivalent conformations of **3**.

3. *HeI photoelectron spectrum of* **3**. The spectrum shown in *Figure 3* features three partially overlapping $\pi$-bands ① to ③ below 10 eV ionization energy. Making use of *Koopmans'* theorem and the experience gained from *Heilbronner*'s investigations of related eight-membered carbocycles with various degrees of unsaturation [16] [17], these bands are readily interpreted on the basis of the qualitative interaction *Scheme 3*. The familiar empirical shifts $\delta A_d$ and $\delta A_t$ of the $\pi$-orbital basis energies may be viewed as inductive effects, the shift $\delta\varepsilon_\sigma$ of the highest $\sigma$-orbital as a consequence of the increase in s-character, both due to further oxidation (*i.e.*

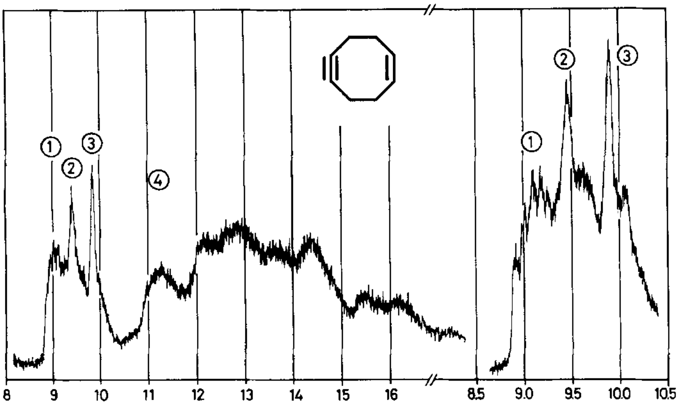
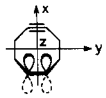
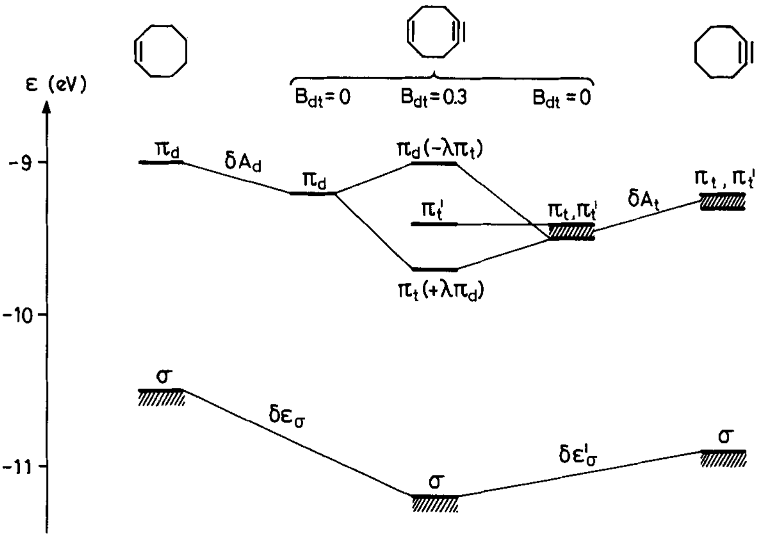


Fig. 3. *He I Photoelectron spectrum of* **3**

Table 1. *Experimental ionization potentials I and calculated orbital energies and coefficients of* **3** (SPINDO, geometry as shown in *Figure 4*)

| | ① | ② | ③ | ④ |
|---|---|---|---|---|
| $I_v$ [eV] | 9.10 ($I_a$ 8.90) | 9.43 | 9.85 | 10.9 |
| $-\varepsilon_J$ [eV] | 10.01 | 10.22 | 10.40 | 11.61 |
| $\psi_J$ | $0.64\pi_d - 0.52\pi_t^x - 0.23\pi_t^z$ | $0.22\pi_d + 0.47\pi_t^x - 0.74\pi_t^z$ | $0.63\pi_d + 0.49\pi_t^x + 0.48\pi_t^z$ | $\sigma$ |
| |  <br>$\pi_d \cong 0.96\pi_d^x + 0.3\pi_d^z$ | <br>$\pi_t^x$ | <br>$\pi_t^z$ | |

*Scheme 3*

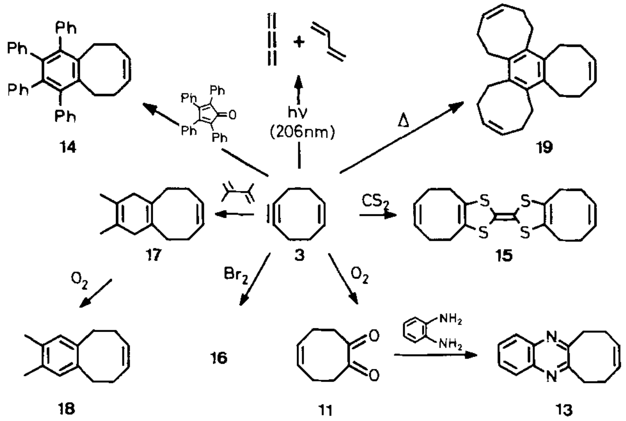


dehydrogenation) of the reference hydrocarbons. The band assignments thus obtained are corroborated by the observed vibrational structure and by the results of semiempirical SPINDO calculations [18] *(Table 1).* The *Franck-Condon*-forbidden appearance of the first $\pi$-band ① with a dominant progression of *ca.* 650 $cm^{-1}$ is similar to that of the first band in the spectrum of norbornadiene [19] [20] which also corresponds to ionization from a molecular orbital constructed by out-of-phase combination of two homoconjugated $\pi$-orbitals. It indicates that the removal of an electron from the homo-antibonding orbital in the ionization process is followed by a skeletal relaxation which decreases the distance between the two $\pi$-systems.

4. *Chemical reactivity of* **3**. The products obtained by reacting **3** with various substrates are shown in *Scheme 4*. All ground-state reactions are initiated by attack at the triple bond and have many analogies in the chemistry of strained cycloalkynes [1] [4] [15]. Where a comparison is possible, the reactivity of **3** is found to be considerably greater than that of **1** or **2**. Apart from the oxidation product **11**, the structure of which has been established by comparing its quinoxaline derivative **13** with an authentic sample [9], the products were identified on the basis of spectroscopic data. Some comments on individual reactions follow; details are given in the experimental part.

(*i*) The photochemical cleavage of **3** to butadiene and butatriene upon direct 206 nm irradiation in solution is paralleled by the behaviour of 1,5-cyclooctadiene and 1,5-cyclooctadiyne (**2**) which yield butadiene [21] and butatriene [4], respectively. Strong fragment peaks are also observed at *m/e* 54 (butadiene) and/or 52 (butatriene) in the mass spectra of the above compounds. Note that all previous photochemical work with 1,5-cyclooctadiene [22] has been carried out with 254 nm light in the presence of triplet sensitizers or transition metal catalysts whereby various isomerization products have been obtained. (*ii*) Attempts to detect chemiluminescence during thermal oxidation of **3** or after exposure of **3** to singlet oxygen

*Scheme 4*



at low temperature have failed. Thus we have not been able to extend the interesting observations of *Turro et al.* [23] with 3,3,6,6-tetramethyl-1-thia-4-cycloheptyne, providing evidence for the occurrence of a chemiluminescent dioxetene intermediate in the oxidation of strained acetylenes. A possible explanation may lie in the fact that the photoexcited luminescence of the dione **11** was too weak to be detected by our conventional instrumentation. (*iii*) The *Diels-Alder* addition to the well-known trapping reagent tetracyclone was used to determine the *in-situ* yield of **3**. Oxidation of recrystallized dihydrazone in the presence of excess tetracyclone gave a 87% yield of the isolated adduct **14**. The overall yield of 30% **14**, obtained from the dione **11** without purification of the dihydrazone, indicates that losses must be mainly due to side reactions in the dihydrazone formation. (*iv*) The rate of *Diels-Alder* addition of **3** to 2,3-dimethylbutadiene at room temperature ($k \cong 10^{-5}\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$) is comparable to that of **2** at 75° under otherwise similar conditions. The high reactivity of **3** towards dienes thus explains the absence of monoadduct during the reaction of **2** with dienes *(Scheme 1)*, as was proposed previously [4]. (*v*) The high reactivity of **3** is also apparent from the reaction with carbon disulfide which is terminated within a few hours at room temperature and yields the expected, carbene-derived product **15**. The reaction rate is comparable to that of 3,3,6,6-tetramethyl-1-thia-4-cycloheptyne and considerably faster than that of **1** [15]. (*vi*) Bromination of **3** has yielded a mixture of several di- and tetrabromides which have not been identified. The main product **16** was a dibromo adduct ($M^+$ 266±2) and its $^1$H-NMR. revealed the presence of a $-CH_2-CH=CBr-$ partial structure (1 H at 6.24 ppm, *t*, $J = 8.5$ Hz) and the absence of $-CHBr-$ (no signal in the range of 2.5 to 6 ppm).

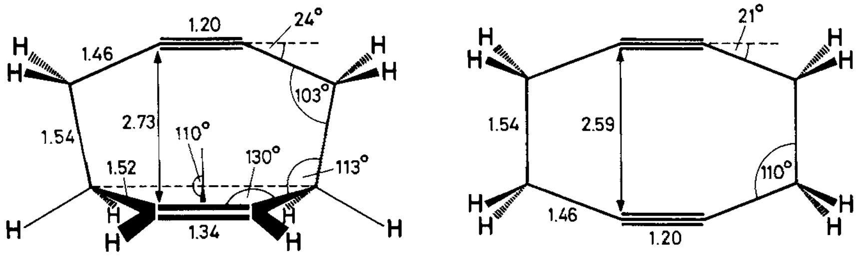
5. *Force field calculations, strain energy.* Molecular models of **3** suggest that the molecule adopts a rather rigid equilibrium conformation of $C_s$-symmetry, in which the carbon atoms of each the $-CH_2-CH_2-C{\equiv}C-CH_2-CH_2-$ and the $-CH_2-CH=CH-CH_2-$ moieties occupy a plane, the two planes intersecting at the two common methylene carbon atoms ($a$ to the double bond) with an inclination of *ca.* 110°. In order to quantify the angle strain present in **3**, a simple strain minimization calculation was performed assuming $C_s$-symmetry, rigid standard bond lengths,

and variable bond angles with harmonic potentials for deviations from standard bond angles of 180° for $C{\equiv}C{-}C$ ($k = 0.063$), 122° for $C{-}CH{=}C$ ($k = 0.105$), and 111° for $C{-}CH_2{-}C$ ($k = 0.121$ kJ · mol$^{-1}$ · degree$^{-2}$) [24]. The potential for the transannular repulsion of the $\pi$-moieties was taken from [4]. The resulting equilibrium structure is shown in *Figure 4*. For comparison, we show the structure of **2** which was obtained by a similar calculation and which is very close to the result of *Römming*'s X-ray structure analysis of **2** [4]. The strain energy of **3**, calculated by the above procedure, amounts to 60 kJ/mol and resides predominantly (36 kJ/mol) in the *cis*-bent triple bond. Together with the heat of formation obtained for the hypothetical strain-free reference system by summing up *Benson*'s group increments [25], we predict $\Delta_f H^{\circ}$ (**3** (g); 298 K) = 280 kJ/mol. This value should be accurate within ±25 kJ/mol, allowing for a 30% error in the calculated strain energy.

A full geometry optimization for **2** and **3** without symmetry restrictions has been carried out upon request by *Allinger* [26], using his 1973 force field with additional parameters to cover acetylenes [27]. This calculation confirms the above assumption of a biplanar structure with $C_s$-symmetry for **3** and the detailed structures are in fair agreement with those shown in *Figure 4*. The largest discrepancy is in the deviations of the triple bonds from linearity which were obtained as 17.7 and 22.7° for **2** and **3**, respectively. A systematic trend of *Allinger*'s force field to underestimate the amount of *cis*-bending in strained acetylenes has been noted previously [28] and, presumably, is due to the fact that all C–C–C bending force constants are assumed to be equal ($k = 0.38$ mdyn · Å · rad$^{-2} \mathrel{\hat{=}} 0.070$ kJ · mol$^{-1}$ · degree$^{-2}$). The heats of formation are calculated as $\Delta_f H^{\circ}$ (**2** (g); 298 K) = 487 and $\Delta_f H^{\circ}$ (**3** (g); 298 K) = 299 kJ/mol. These values include strain energies of 121 (**2**) and 85 (**3**) kJ/mol and are in satisfactory agreement with our previous estimates (above and [4]).

**Conclusions.** - The highly strained, hitherto unknown hydrocarbon cyclooct-1-en-5-yne (**3**) is stable at −15° in the absence of oxygen. NMR.-spectroscopic data and force field calculations of **3** have consistently provided evidence for the existence of two equivalent stable conformers of $C_s$-symmetry which rapidly interconvert in solution at room temperature. The free energy of activation for this isodynamical process amounts to *ca.* 42 kJ/mol. The strain energy of the equilibrium structures is estimated to 75±20 kJ/mol, residing largely in the *cis*-bending of the triple bond. Its deviation from linearity (*ca.* 24°) appears to be markedly greater than in cyclooctyne (**1**, 21°) or 1,5-cyclooctadiyne (**2**, 21°). In contrast to the common reactivity ordering olefins > acetylenes (comparable chemical environments

**3**



**2**

Fig. 4. *Equilibrium structures for* **2** *and* **3** *obtained after bond angle strain minimization with rigid standard bond lengths*

provided), the reactants investigated invariably attack **3** at the triple bond and, where a comparison is possible, the reaction rates are considerably faster than with **1** or **2**. This is reasonable, because the strain manifested by increasing in-plane deformation of the unsaturated moieties is directly released only by attack at the acetylenic in-plane $\pi$-orbitals. Thus, the reactivity of triple bonds is very sensitive to *cis*-bending, while that of double bonds is not markedly enhanced by in-plane deformation[2]).

## Experimental Part

UV./VIS. absorption maxima (or shoulders (*sh*)) are given in nm (log$\varepsilon$), IR. spectra in $cm^{-1}$ (intensity designations weak (*w*), medium (*m*), strong (*s*)). - 100 MHz $^1H$-NMR. and 25.2 MHz $^{13}C$-NMR. spectra are quoted in ppm relative to internal TMS. (splitting patterns designated as singlet (*s*), doublet (*d*), triplet (*t*), ... multiplet (*m*); coupling constants in Hz). - The molecular ion ($M^+$) and dominant fragment ion peaks in the mass spectrum are given in units of *m/e* (percent relative intensity). The synthesis and subsequent handling of **3** was carried out *in vacuo* ($10^{-3}$ Torr).

*Synthesis of cyclooct-(5Z)-ene-1,2-dione* (**11**). The synthesis of **11** has been described by *Yates et al.* [9]. In order to prevent the ready decomposition of its precursor diol **10** during hydrolysis and work-up, the procedure [9] was modified as follows: An ice-cooled solution of sodium hydroxide (150 g in 300 ml water) was cautiously added to the ice-cooled and stirred raw product (160 g) resulting from the oxidation of 1,5-cyclooctadiene (114 ml), keeping the temperature of the reaction mixture below 45° during, and at 45° for half an hour after the addition. The diol **10** was then extracted by washing with five portions of warm ethyl acetate (300 ml each, 45°). The extracts were combined, dried, evaporated, and the residue was vacuum-distilled (94 to 96°/0.3 Torr) to give 54.4 g (42%) of (5Z)-cyclooctene-(1$\alpha$,2$\beta$)-diol (**10**) as a colourless oil.

The spectroscopic data for **10** and **11** were in agreement with those given in [9]. The first bands in the photoelectron spectrum of **11** ($I_v$ 9.20, 9.79, and 11.05 eV) are attributed to ionization from the in-phase combination of the oxygen lone pairs ($n_+$), the double bond $\pi$-orbital ($\pi$), and the out-of-phase lone pair combination ($n_-$), respectively, by analogy to the assignments in related dicarbonyl compounds [29].

*Hemiacetal of* **11**. The dione **11** is readily converted to its mono-hemiacetal **12** in alcoholic solvents. The reaction is acid-catalysed but proceeds at a rate of at least $10^{-3}s^{-1}$ (25°) even in highly pure methanol. The equilibrium constant $K=[\mathbf{12}]/[\mathbf{11}]$ was determined as $4.5 \pm 1$ by UV. and NMR. analysis at room temperature. The hemiacetal is stable as a solid but decomposes upon melting to **11** and methanol above 35°. It is reconverted to **11** by vacuum distillation or upon standing in aprotic solvents. - UV. (**12**, methanol): 303 (1.2). - $^1H$-NMR. (**12**, $CDCl_3$): 1.5-1.9 (*m*, 2 H); 2.0-3.1 (complex *m*, 6 H); 3.28 (*s*, 3 H); 4.0 (br. *s*, 1 H); 5.4-5.8 (*m*, 2 H).

*Synthesis of cyclooct-(5Z)-ene-1,2-dione dihydrazone.* A cooled solution of the dione **11** (1 g in 4 ml ethanol, −20°) was added dropwise to a stirred solution of hydrazine hydrate (0.92 g in 4 ml ethanol, −20°). The mixture was then allowed to warm up to room temperature and stirred for half an hour. Ethanol, water, and excess hydrazine were evaporated (25°/0.2 Torr), the residue triturated in chilled ether, filtered and dried to give 0.7 g of white powder. This raw product was used as such for the synthesis of **3**. Recrystallization for analytical purposes by dissolution in benzene ($\leqslant$40°) and standing for two days at room temperature afforded 0.29 g (24%) of cyclooct-5-ene-1,2-dione dihydrazone as colourless prisms, m.p. 125-127°. - $^1H$-NMR. ($CDCl_3$): 2.1-2.6 (*m*, 8 H); 5.2 (br. *s*, 4 H); 5.74 (symmetric *m*, 2 H). - MS.: 166 (10), 150 (80), 137 (40), 120 (55), 109 (80), 93 (90), 91 (90), 84 (80), 81 (70), 79 (100), 77 (70), 67 (100).

$C_8H_{14}N_4$ (166.23) Calc. C 57.80 H 8.49% Found C 57.75 H 8.38%

*Synthesis of cyclooct-(1Z)-en-5-yne* (**3**). Degassed solutions of lead tetraacetate (4 g) in methyl bromide (30 ml) and cyclooct-5-ene-1,2-dione dihydrazone (0.7 g) in the minimum amount of methyl bromide required (*ca.* 100 ml) were united at once and shaken vigorously. After the evolution of nitrogen

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[2]) *Added in proof:* A short communication by *Meier et al.* [32] has just appeared which reports the isolation of cyclooct-1-en-3-yne and MINDO/2 calculations of three isomeric cyclooctenynes including **3**.

had ceased, the mixture was cooled to −77° and the solvent evaporated. The volatile components of the residue were then evaporated at −10° into a tube containing 1 g of dry potassium carbonate and 4 ml of degassed pentane, warmed to 10°, and shaken to ensure complete neutralization of the acetic acid present. The volatiles were vacuum transferred to a new tube where a drop of water separated upon warming. The organic layer was decanted, the solvent evaporated at −77°, and the residue resublimed repeatedly from bulb to bulb yielding *ca.* 150 mg (30%) of pure **3** as colourless crystals, m.p. −10°. - UV. (pentane): end absorption only. - Far UV. (gas phase [30]): 188 (rel. int. 0.3), 172 (0.2), 159 (0.7), 157 (0.7), 139 (0.9), 128 (1.0). - IR. (gas phase): 3028*m*, 2960*s*, 2950*s*, 2875*m*, 1448*m*, 760*m*, 717*m*. - $^1$H-NMR. ($CDCl_3$): 2.1–2.3 (*m*, 4 H); 2.5–2.7 (*m*, 4 H); 5.7–6.1 (symmetric *m*, 2 H); the spectrum is displayed in *Figures 1* and *2* and analysed in the accompanying text. - $^{13}$C-NMR. ($CDCl_3$): 19.2 (*t*, $J = 135$); 30.8 (*t*, $J = 128$); 100.4 (*s*); 131.4 (*d*, $J = 152$); assignments are given in the text. - MS.: 107 (7), 106 ($M^+$, 64), 105 (30), 103 (11), 92 (10), 91 (100), 79 (29), 78 (40), 77 (21), 67 (7), 66 (12), 65 (21), 63 (10), 54 (30), 53 (14), 52 (85), 51 (30), 50 (18), 41 (11), 39 (47), 27 (24).

In situ *trapping of* **3** *by tetracyclone.* Degassed solutions of the dihydrazone (0.1 g) and tetracyclone (0.5 g) in methylene chloride (50 ml) and lead tetraacetate (0.61 g) in methylene chloride (15 ml) were united at room temperature and shaken for 2 min. The mixture was extracted twice with water (50 ml), dried, and evaporated to dryness. The residue was chromatographed on neutral alox with petrol ether/benzene 2:1. The first eluate was collected and sublimed (170°/$10^{-2}$ Torr) yielding 0.24 g of the adduct 5,6,9,10-tetrahydro-1,2,3,4-tetraphenylbenzocyclooctene (**14**) (87%) as a white powder, m.p. 209°. - $^1$H-NMR. ($C_6D_6$): 2.1–2.4 (*m*, 4 H); 2.92 (*t*, 4 H, $J = 7$); 5.64 ± 0.2 (symmetric *m*, 2 H); 6.6–7.3 (complex *m*, 20 H). - MS.: 463 (39), 462 ($M^+$, 100), 433 (13), 407 (13).

*Photolysis of* **3**. A degassed, $10^{-2}$M solution of **3** in pentane was irradiated for 1 h by unfiltered light (predominantly 206 nm) from a home-built iodine discharge lamp [31]. The products were identified as an approximately equimolar mixture of butadiene and butatriene by comparison with authentic spectra [4].

*Pyrolysis of* **3**. A degassed, *ca.* 0.1M solution of **3** in hexadeuterobenzene (0.5 ml in a sealed NMR. tube) was heated to 75° in the cavity of an NMR. spectrometer. After 14 h the changes in the NMR. spectrum indicated *ca.* 80% conversion of **3** to its trimer **19**. The solvent was evaporated, the residue recrystallized from ethanol and sublimed (120°/$10^{-2}$ Torr) to yield 5 mg tris(cycloocta-1,5-dieno)benzene (**19**) as a white powder, m.p. 138°. - UV. (hexane): 280 (*sh*, 2.26), 274 (2.40), 232 (*sh*, 4.03), 214 (4.54). - $^1$H-NMR. ($C_6D_6$): 2.1–2.5 (*m*, 12 H); 2.86 (*t*, 12 H, $J = 7$); 5,41 ± 0.2 (symmetric *m*, 6 H). - MS.: 319 (28), 318 ($M^+$, 100), 303 (30), 290 (35), 289 (60), 264 (50), 249 (80).

*Reaction of* **3** *with oxygen.* A solution of **3** (*ca.* 10 mg) in methylene chloride (5 ml) was saturated with oxygen (3 atm.) and left overnight. A mass spectrum of the residue after evaporation of the solvent indicated the presence of the dione **11** which, for unambiguous identification, was converted to 6,7,10,11-tetrahydro-(*Z*)-cycloocta[b]quinoxaline (**13**) [9] and compared with an authentic sample.

Diels-Alder *addition of* **3** *to 2,3-dimethyl-1,3-butadiene.* Deuteriochloroform (0.5 ml), TMS. (0.02 ml), diene (0.1 ml), and **3** (*ca.* 30 mg) were vacuum transferred to an NMR. tube which was sealed and kept at room temperature. The reaction was monitored by intermittent NMR. analysis. After three days more than 90% of **3** were consumed. Solvent and excess diene were evaporated and the residue sublimed (80°/$10^{-2}$ Torr) to yield 30 mg of 2,3-dimethyl-1,4,5,6,9,10-hexahydrobenzocyclooctene (**17**) which was readily oxidized to 2,3-dimethyl-5,6,9,10-tetrahydrobenzocyclooctene (**18**) upon standing in aerated solution. - M.p. (**18**) 45°. - $^1$H-NMR. (**17**, $CCl_4$): 1.56 (*s*, 6 H); 2.26 (br. *s*, 8 H); 2.46 (br. *s*, 4 H); 5.35–5.50 (*m*, 2 H). - $^1$H-NMR. (**18**, $CDCl_3$): 2.16 (*s*, 6 H); 2.2–2.7 (*m*, 4 H); 2.90 (*t*, 4 H, $J = 7$); 5.4–5.6 (*m*, 2 H); 6.82 (*s*, 2 H). - MS. (**17**): 188 (50), 173 (20), 159 (25), 145 (55), 119 (100); MS. (**18**): 186 (90), 171 (45), 157 (55), 132 (100).

*Reaction of* **3** *with carbon disulfide.* A degassed solution of **3** (*ca.* 30 mg) in $CS_2$ (0.5 ml) was left at room temperature. Within an hour the solution took on an orange colour which did not become more intense after standing overnight. The solvent was evaporated and the residue was chromatographed on silica with chloroform. The orange eluate was collected and recrystallized from carbon tetrachloride to yield 20 mg of bis(cycloocta-1,5-dieno[*d,d'*]-2,2'-bi(1,3-dithiolylidene) (**15**) as red crystals, m.p. 204°. - IR. ($CHCl_3$): 3010*s*, 2950*m*, 2900*s*, 2840*m*, 1660*w*, 1610*w*. - $^1$H-NMR. ($CDCl_3$): 2.4 (br. *s*, 16 H); 6.5 (symmetric *m*, 4 H). - MS.: 366 (22), 365 (26), 364 ($M^+$, 100), 310 (41), 256 (19), 226 (44), 172 (33).

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