

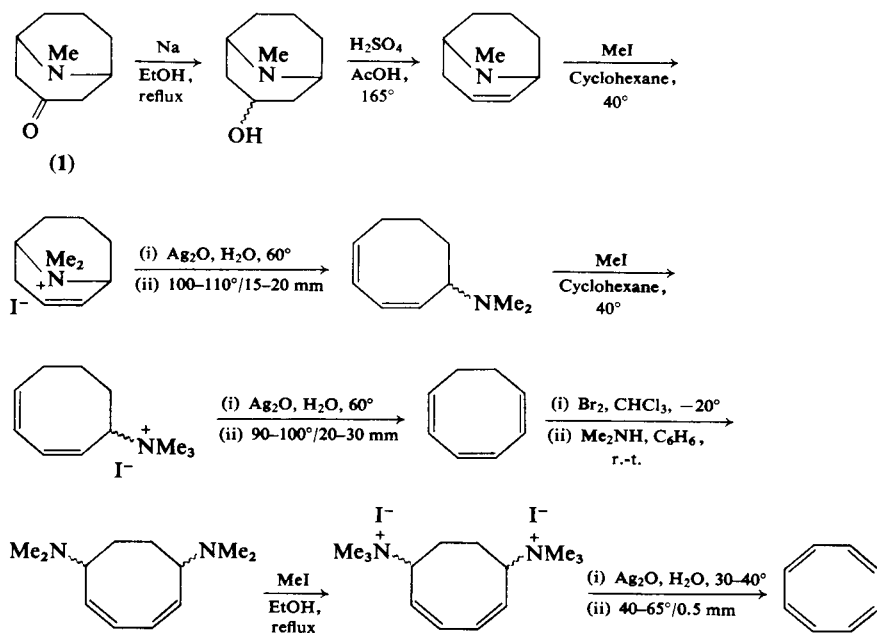
## 1

## Cyclo-octatetraene

## 1. Formation

Cyclo-octatetraene was first described in 1911 by Willstätter and Waser,<sup>1</sup> who obtained it from pseudo-pelletierine (**1**), an alkaloid from the bark of the pomegranate tree, by a lengthy degradation proceeding *via* cyclo-octa-1,3,5-triene (see also ref. 2). The resulting sample of COT probably contained *ca.* 30% of styrene,<sup>3</sup> and its authenticity did not go unchallenged (for a review of the evidence, see ref. 4). However, the original reaction sequence was repeated some thirty-six years later by Cope and Overberger<sup>3,5</sup> (scheme 1), and Willstätter's claim was completely vindicated.

Scheme 1



This type of approach to COT may be simplified by starting from the readily available cyclo-octa-1,5-diene, but the introduction of the additional double

Cambridge University Press

978-0-521-10565-1 - The Chemistry of Cyclo-Octatetraene and its Derivatives

G. I. Fray and R. G. Saxton

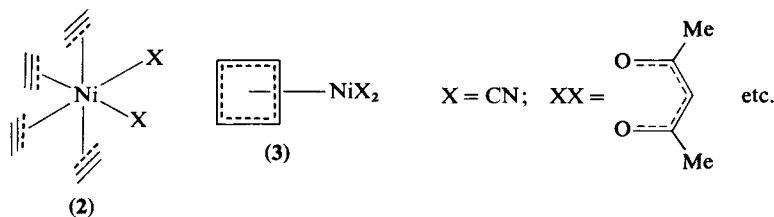
Excerpt

[More information](#)

## 2 Cyclo-octatetraene

bonds by means of the Hofmann elimination procedure,<sup>6,7</sup> or by dehydrobromination,<sup>8-10</sup> results in poor yields of a product which is contaminated with styrene, benzocyclobutene etc.

In 1940, the important discovery that COT could be produced by the cyclo-tetramerisation of acetylene was made in the laboratories of Badische Anilin- & Soda-Fabrik AG, by Reppe *et al.*<sup>11</sup> The reaction is best carried out (up to 70% conversion) in dry tetrahydrofuran or dioxan at 85–90° and a pressure of 15–25 atmospheres, in the presence of nickel(II) compounds such as the cyanide or chelate 'ato' complexes from acetylacetonate, acetoacetic esters, salicylaldehyde, *N*-alkylsalicylaldehydes etc.<sup>11-15</sup> (a much less efficient conversion results from the use of  $(\text{CH}_2=\text{CH}.\text{CN})_2\text{Ni}$ <sup>16</sup>). The process has been reviewed,<sup>17-19</sup> and Schrauzer<sup>15,18</sup> has proposed a mechanism involving an intermediate octahedral nickel complex (2) (but see appendix). (For a discussion of bonding in this type of complex, see refs. 20, 21. An earlier hypothesis proposed the intermediacy of a cyclobutadiene complex (3)<sup>22</sup>.)



Among the by-products of the Reppe process are benzene, styrene, naphthalene, azulene, *Z*-1-phenylbuta-1,3-diene, vinylcyclo-octatetraene, and a  $\text{C}_{12}\text{H}_{12}$  fraction of unknown constitution.<sup>23-26</sup>

Octadeuteriocyclo-octatetraene may be prepared by similar cyclo-tetramerisation of dideuterioacetylene.<sup>27</sup>

COT has been identified as one of the products of the thermal polymerisation of acetylene,<sup>28,29</sup> and very low yields of COT result from u.v. irradiation of acetylene.<sup>30,31</sup>

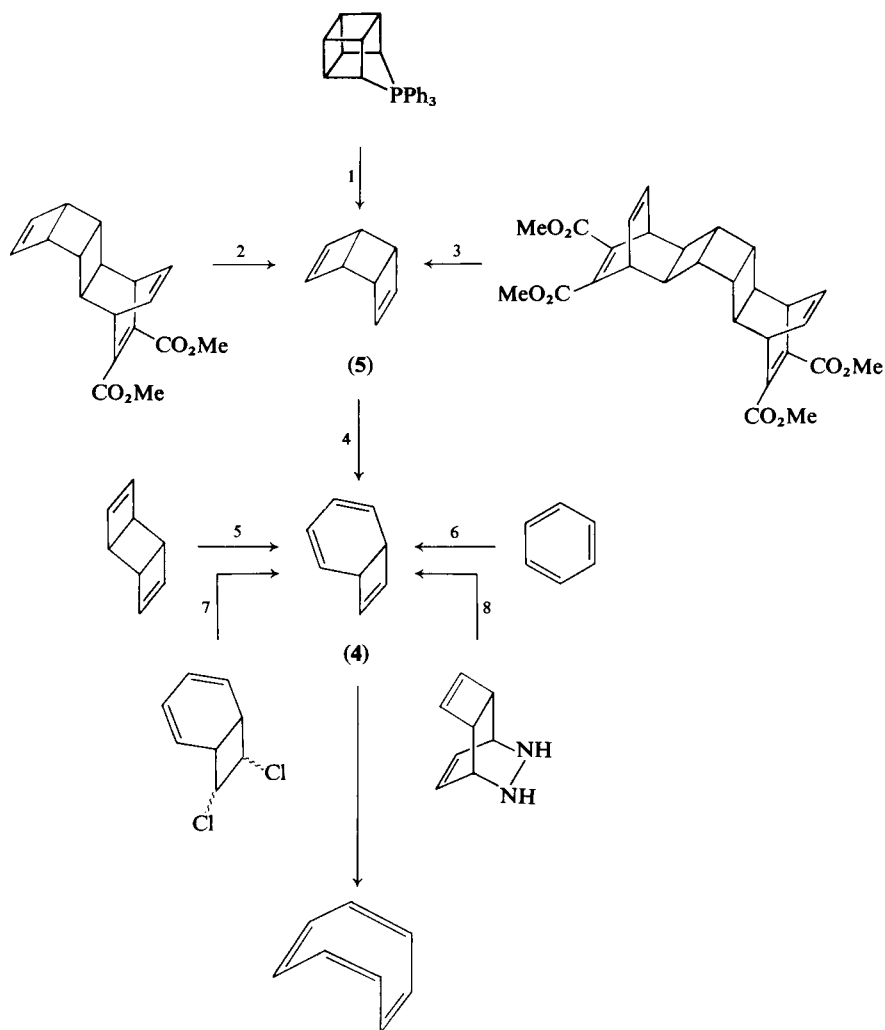
COT is also formed by various isomerisation processes occurring in other  $\text{C}_8\text{H}_8$  compounds. Reactions which generate bicyclo[4.2.0]octa-2,4,7-triene (4), unless carried out at low temperatures,<sup>32</sup> lead to COT *via* valence isomerism (see p. 10); examples are given in scheme 2.

Other skeletal rearrangements leading to COT are outlined in schemes 3 and 4.

Additionally, COT is a minor photo-product of basketene (6)<sup>55</sup> and of the dimethyl acetylenedicarboxylate adduct (7),<sup>56</sup> and it has been detected amongst the pyrolysis products of the  $\beta$ -lactone (8)<sup>57</sup> and of  $\alpha$ -cellulose.<sup>58</sup>

Finally, COT has been identified as one of the constituents responsible for the odour of tomatoes,<sup>59</sup> and may therefore be a natural product!

Scheme 2



| Reaction | Reagents and conditions   | Yield (%)       | Ref.     |
|----------|---|-----------------|----------|
| 1        | 120°  | 85 <sup>a</sup> | 33       |
| 2        | 140–160°  | —               | 34       |
| 3        | ca. 150°  | —               | 34       |
| 4        | (>100°), 90–121°  | —               | (35), 36 |
| 5        | { <i>o</i> -Dichlorobenzene, 140°<br>or e.g. AgBF <sub>4</sub> , Me <sub>2</sub> CO, reflux | 100             | 35       |
| 6        | HC≡CH, <i>hν</i>  | 100             | 37       |
| 7        | NaI, NaHSO <sub>3</sub> , Me <sub>2</sub> CO, r.-t. → 50°                                   | (Very low)      | 38       |
| 8        | MnO <sub>2</sub> , n-hexane, r.-t.  | 35              | 39       |
|          |   | 75–80           | 40       |

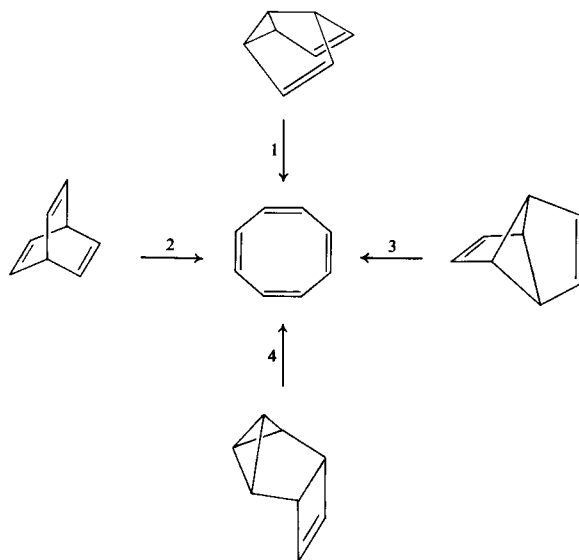
<sup>a</sup> Mixture of (5) and COT (4:1).

Cambridge University Press

978-0-521-10565-1 - The Chemistry of Cyclo-Octatetraene and its Derivatives

G. I. Fray and R. G. Saxton

Excerpt

[More information](#)4 *Cyclo-octatetraene*

| Reaction | Reagents and conditions  | Yield (%) | Ref.           |
|----------|--|-----------|----------------|
| 1        | { AgNO <sub>3</sub> , MeOH(aq.), 80°<br>or 427°/30 mm (flow system)  | 100<br>56 | 41<br>(42), 43 |
| 2        | <i>hν</i> , methylcyclohexane  | 20        | 44             |
| 3        | <i>hν</i> (Pyrex), e.g. isopentane, -60°                             | Up to 29  | 45             |
| 4        | { 400–500°<br>or e.g. AgClO <sub>4</sub> , Me <sub>2</sub> CO, r.-t. | —<br>—    | 46<br>46       |

## 2. Purification

The purification of COT by fractional distillation and low-temperature crystallisation has been described in detail.<sup>60</sup>

For separation by liquid–solid column chromatography, see ref. 44.

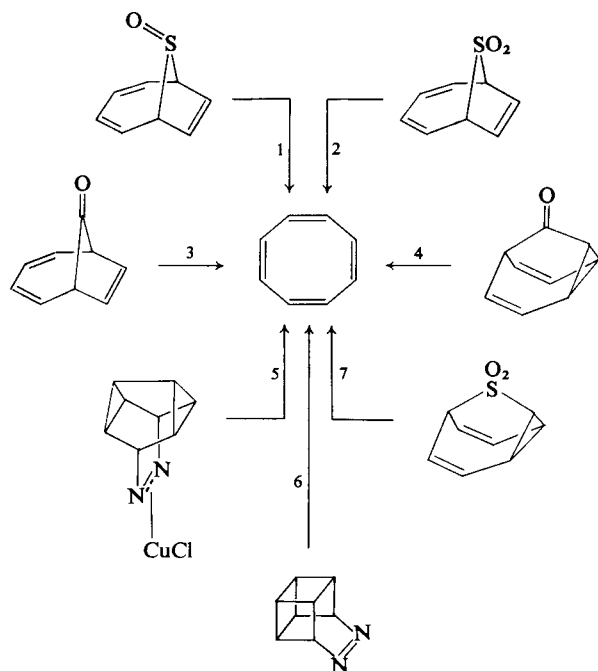
For the use of gas–liquid chromatography, see e.g. refs. 9, 40, 44, 49; for other gas-chromatographic data see refs. 61, 62.

COT may also be purified *via* its silver nitrate complex (COT)<sub>2</sub>(AgNO<sub>3</sub>)<sub>3</sub> (see p. 51), from which it is readily regenerated by treatment with aqueous sodium chloride.<sup>63</sup>

COT forms an inclusion complex with thiourea,<sup>64</sup> but no use of this property appears to have been made.

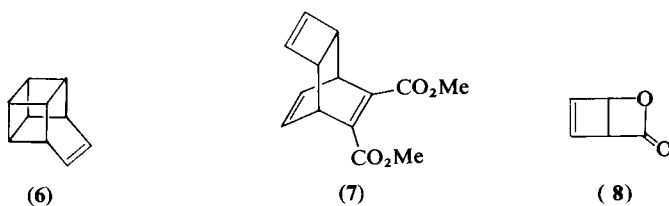
COT is somewhat sensitive to air and light, and is best stored in the dark below room-temperature, in the presence of a free-radical inhibitor such as hydroquinone. Even so, samples of COT which have been kept for some time inevitably contain dimeric and polymeric material (see pp. 12–13, 34).

Scheme 4



| Reaction | Reagents and conditions   | Yield (%) | Ref.         |
|----------|---|-----------|--------------|
| 1        | <i>hν</i>   | —         | 47           |
| 2        | { 345° (g.l.c.)<br>or <i>hν</i> (Corex), Me <sub>2</sub> CO, Et <sub>2</sub> O <sup>a</sup> | 100       | 48           |
| 3        | <i>hν</i> (Pyrex), Et <sub>2</sub> O or THF   | 80–82     | (50), 51, 52 |
| 4        | <i>hν</i>   | —         | 50           |
| 5        | 25°   | 100       | 41           |
| 6        | <i>hν</i>   | (Low)     | 53           |
| 7        | 240° (flow system)  | 100       | 54           |

<sup>a</sup> Conditions used for 1,4-dideuteriocyclo-octatetraene (40%).<sup>49</sup>



Cambridge University Press

978-0-521-10565-1 - The Chemistry of Cyclo-Octatetraene and its Derivatives

G. I. Fray and R. G. Saxton

Excerpt

[More information](#)6 *Cyclo-octatetraene*

## 3. Physical properties

COT is a yellow liquid, with a strong distinctive odour.

|  |  |                  |                     |                            |
|--|--|------------------|---------------------|----------------------------|
| Boiling-point (°C)   | 142–143<br>48<br>42–42.5                       | Pressure (mm Hg) | 760<br>31<br>17     | Ref. 11<br>65<br>11        |
| Melting-point (°C)   | –4.7<br>–4.5 to –3.5                           |                  |                     | 27, 66<br>63               |
| Triple-point (K)   | 268.48   |                  |                     | 66                         |
| Density (g cm <sup>-3</sup> )                                    | 0.9382<br>(0.9206), 0.9209<br>0.9196<br>0.9117 | Temperature (°C) | 0<br>20<br>25<br>30 | 11<br>(11), 60<br>60<br>60 |
| Viscosity (cP)   | 1.42<br>1.30<br>1.18                           | Temperature (°C) | 20<br>25<br>30      | 60<br>60<br>60             |
| Heat capacity (12–330 K): see ref. 66                            |  |                  |                     |                            |
| Vapour pressure (0–75 °C): see ref. 66                           |  |                  |                     |                            |
| Heat of fusion (cal mol <sup>-1</sup> )                          | 2694.6   |                  |                     | 66                         |
| Heat of combustion (25 °C) (kcal mol <sup>-1</sup> )             | –1084.9<br>–1086.5                             |                  |                     | 67<br>68                   |
| Heat of hydrogenation (25 °C) (kcal mol <sup>-1</sup> )          | –97.96   |                  |                     | 69                         |
| Refractive index (N <sub>D</sub> ) <sup>a</sup>                  | 1.5379<br>(1.5348), 1.5350<br>1.5323           | Temperature (°C) | 20<br>25<br>30      | 60<br>(63), 60, 69<br>60   |
| <sup>a</sup> For measurements at other wavelengths, see ref. 60. |  |                  |                     |                            |
| Dielectric constant (20 °C)                                      | 2.74   |                  |                     | 11                         |
| First ionisation potential (adiabatic) <sup>a</sup> (eV)         | 7.99<br>8.0<br>8.04<br>8.06                    |                  |                     | 70<br>71<br>72<br>73       |
| <sup>a</sup> For higher ionisation potentials, see refs. 71, 72. |  |                  |                     |                            |
| Electron affinity (kcal mol <sup>-1</sup> )                      | 13.3   |                  |                     | 74                         |
| Half-wave reduction potentials: see e.g. refs. 65, 75–82         |  |                  |                     |                            |
| Magnetic susceptibility (cm <sup>3</sup> mol <sup>-1</sup> )     | –0.0000539                                     |                  |                     | 83, 84                     |
| Magnetic rotation (μrad)   | 1009   |                  |                     | 85                         |

Cambridge University Press

978-0-521-10565-1 - The Chemistry of Cyclo-Octatetraene and its Derivatives

G. I. Fray and R. G. Saxton

Excerpt

[More information](#)

## Purification 7

The following have been calculated from thermochemical data:

|   |                    |        |         |
|---|--------------------|--------|---------|
| Heat of vaporisation (25°C) (cal mol <sup>-1</sup> )  | 10300              |        | Ref. 66 |
| Entropy (cal deg <sup>-1</sup> mol <sup>-1</sup> )  | (Liquid, 25°C)     | 52.65  | 66      |
|   | (Gas, 25°C, 1 atm) | 78.10  | 66      |
| Heat of formation (kcal mol <sup>-1</sup> )   | (Liquid, 25°C)     | 60.82  | 68      |
|   | (Gas, 25°C)        | 71.0   | 86, 87  |
|   |                    | 71.1   | 88, 89  |
|   |                    | 71.12  | 90      |
|   |                    | 71.3   | 91      |
|   | 71.9               | 69     |         |
| Heat of isomerisation to styrene (kcal mol <sup>-1</sup> )                                      | (Liquid, 25°C)     | -36.10 | 68      |
|   | (Gas, 25°C)        | -36.3  | 69      |
| Empirical (thermochemical) resonance energy<br>(stabilisation energy) (kcal mol <sup>-1</sup> ) |                    | 2.4    | 69      |
|   |                    | 3.0    | 92      |
|   |                    | 3.3    | 93      |
|   |                    | 3.6    | 69      |
|   |                    | 4.8    | 67      |

For other calculations, see table 5, p. 11.

*U.v. spectrum.* COT exhibits a broad weak absorption band with a maximum near 280 nm (table 1), which tails into the visible region;<sup>94,95</sup> there is strong 'end-absorption', with a shoulder at *ca.* 205 nm<sup>95,96</sup> ( $\epsilon$  20000<sup>97</sup>). The absorption curve is reproduced in refs. 60, 94, 98. (Measurements have also been made in the gas phase<sup>94,95</sup>.)

Table 1

| Solvent           | $\lambda_{\max}$ . (nm) | $\epsilon$ | Ref. |
|-------------------|-------------------------|------------|------|
| MeOH              | 280                     | 350        | 94   |
| EtOH              | 280                     | 435        | 94   |
| n-Heptane         | 280                     | 235        | 94   |
| CHCl <sub>3</sub> | 282                     | 200        | 99   |
| Cyclohexane       | 283                     | 255        | 94   |
| Iso-octane        | 283                     | 250        | 98   |
| CCl <sub>4</sub>  | 288                     | 320        | 94   |

*I.r. spectrum.* The C=C stretching vibration in COT gives rise to an absorption band with  $\nu_{\max}$ . (liquid film) 1634,<sup>99</sup> 1635<sup>27</sup> cm<sup>-1</sup>. The spectrum is reproduced in refs. 27, 60; for complete lists of the principal absorption maxima, see refs. 27, 99. (Measurements have also been made in the gas phase<sup>27,99</sup>.)

*Raman spectrum.* See refs. 27, 100, 101.

Cambridge University Press

978-0-521-10565-1 - The Chemistry of Cyclo-Octatetraene and its Derivatives

G. I. Fray and R. G. Saxton

Excerpt

[More information](#)

## 8 Cyclo-octatetraene

*N.m.r. spectra.* The  $^1\text{H}$  n.m.r. spectrum of COT shows a singlet resonance at  $-341$  Hz relative to tetramethylsilane, i.e. at  $\tau$  4.32 (60 MHz; neat liquid).<sup>102</sup>

For the p.m.r. of solid COT, see ref. 103.

The  $^1\text{H}$  n.m.r. spectrum is temperature-dependent with respect to the  $^{13}\text{C}$  satellites of the proton signal, owing to the conformational mobility of the molecule (see p. 9). At very low temperatures these satellites are essentially double doublets; for the coupling constants, see table 2.

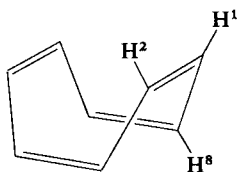


Table 2

| $J(\text{H}^1\text{-H}^2)$ (Hz) | $J(\text{H}^1\text{-H}^8)$ (Hz) | Ref. |
|---------------------------------|---------------------------------|------|
| 11.4                            | ca. 2.5                         | 104  |
| 11.48                           | 3.87                            | 105  |
| 11.8                            | —                               | 106  |

From the  $^{13}\text{C}$  n.m.r. spectrum,  $J(^{13}\text{C}\text{-H}) = 155$  Hz.<sup>107</sup>

The presence of a weak paramagnetic ring-current in COT has been inferred from measurements of solvent shifts.<sup>108</sup>

*Mass spectrum.* The major ions in the mass spectrum of COT, together with their relative abundances and appearance potentials, are listed in ref. 73.

For the doubly-charged ion mass spectrum of COT, see ref. 109.

For the collisional activation spectrum of field-ionised COT, see ref. 110.

*Photo-electron spectrum.* See refs. 71, 72, 111, 112.

*Trapped electron impact spectrum.* See ref. 113.

For electron attachment studies see refs. 114, 115.

*Magnetic circular dichroism.* The MCD curve of COT is reproduced in ref. 98.

### 4. Structure

X-ray<sup>116</sup> and electron diffraction<sup>117-119</sup> studies of COT show that the eight-membered ring exists in a non-planar 'tub' form ( $D_{2d}$  symmetry), with the bond lengths and angles listed in tables 3 and 4.

Although the non-planarity of COT in its ground state prevents *substantial* overlap of the adjacent  $\pi$ -orbitals, certain through-bond and through-space interactions may exist.<sup>72, 85, 87</sup>

The observed u.v. absorption (see p. 7) has been explained on the basis of interactions between the excited  $\pi$ -systems.<sup>121, 122</sup>



Cambridge University Press

978-0-521-10565-1 - The Chemistry of Cyclo-Octatetraene and its Derivatives

G. I. Fray and R. G. Saxton

Excerpt

[More information](#)

Structure 9

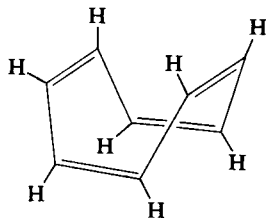


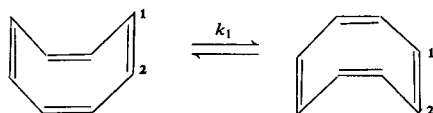
Table 3

| Bond | Length (Å) | Ref. |
|------|------------|------|
| C=C  | 1.330      | 116  |
|      | 1.334      | 118  |
|      | 1.340      | 119  |
| C—C  | 1.456      | 116  |
|      | 1.462      | 118  |
|      | 1.476      | 119  |
| C—H  | 1.090      | 118  |
|      | 1.100      | 119  |

Table 4

|  |        | Ref. |
|--|--------|------|
| Angle $\begin{array}{c} \text{C} \\ \text{C}=\text{C} \\ \text{C} \end{array}$             | 126.1° | 119  |
|  | 126.5° | 118  |
|  | 126.8° | 116  |
| Angle $\begin{array}{c} \text{C} \\ \text{C}=\text{C} \\ \text{H} \end{array}$             | 117.6° | 119  |
|  | 118°   | 118  |
| Torsion angle around $\begin{array}{c} \text{C}=\text{C} \\ \text{C}-\text{C} \end{array}$ | 56°    | 116  |
|  | 58°    | 120  |

*Conformational inversion and valence tautomerism.* At ordinary temperatures, the tub-shaped COT molecule undergoes rapid ring-inversions (see e.g. ref. 123).



This process may be studied in substituted COTs by variable-temperature n.m.r. spectroscopy (see p. 94); for calculations of the energy barrier, see refs. 124–127.

In addition to this conformational change, two kinds of valence tautomerism occur. The first involves bond-shift in the eight-membered ring, the single and double bonds exchanging their positions.

Cambridge University Press

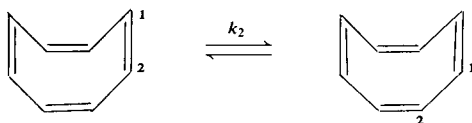
978-0-521-10565-1 - The Chemistry of Cyclo-Octatetraene and its Derivatives

G. I. Fray and R. G. Saxton

Excerpt

[More information](#)

## 10 Cyclo-octatetraene



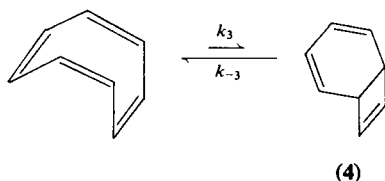
For measurements of the rate constant  $k_2$ , see refs. 104, 106, 128, 129 ( $E_a = 10.9$ ,<sup>129</sup>  $14.5$ <sup>104</sup> kcal mol<sup>-1</sup>;  $\Delta G^\ddagger = 13.3$ ,<sup>104</sup>  $13.7$ <sup>106</sup> kcal mol<sup>-1</sup>).

It is generally assumed that the ring-inversion and bond-shift processes occur *via* the planar transition states (**A**) and (**B**) respectively, (**A**) containing alternate double and single bonds (alternating bond lengths,  $D_{4h}$  symmetry), but (**B**) having  $D_{8h}$  symmetry (equal bond lengths). Theoretical studies<sup>125, 127, 130–133</sup> predict that structure (**A**) should be more stable than the



delocalised form (**B**) (which is 'anti-aromatic'). It follows that inversion should proceed more rapidly than bond-shift, and indeed this is found for substituted COTs in which it is possible to discriminate between the two processes (see p. 94).

The second type of valence tautomerism displayed by COT results in a low concentration (*ca.* 0.01% at 100°) of bicyclo[4.2.0]octa-2,4,7-triene (**4**)<sup>134–136</sup> (a disrotatory  $6\pi$  electrocycloisomerisation is thermally allowed by the Woodward–Hoffmann rules).



For values of  $k_3$ , see refs. 128, 136 ( $E_a = 27.2$  kcal mol<sup>-1</sup>,<sup>128</sup>  $\Delta H^\ddagger = 27.4$ ,<sup>135</sup>  $28.1$ <sup>136</sup> kcal mol<sup>-1</sup>); for  $k_{-3}$ , see ref. 128 ( $E_a = 18.7$  kcal mol<sup>-1</sup><sup>32</sup>).

The theoretical importance of COT as [8]annulene has led to numerous calculations of various aspects of its structure and properties (table 5) (for general discussions, see e.g. refs. 137–139). Calculation of the properties of the lowest  $\pi \rightarrow \pi^*$  triplet state of COT leads to the conclusion that it may be regarded as 'aromatic'.<sup>154</sup>