# The Three Dimensional Structure of all-*cis*-Diepoxy[15]annulenone and some Implications from the Structure

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An *X*-ray structural analysis of all-*cis*-diepoxy[15]annulenone (**1**) revealed that (**1**) exists in two different conformations, each of which possesses a saucer-like three-dimensional geometry, like that of the polyaromatic 14π hydrocarbon corannulene (**5**).

Diepoxy[15]annulenone (**1**),[1a,b] a higher homologue of tropone, is of interest, since it produces mono-*trans* annulenylium ion (**3**) as the major product on protonation [*via* (**2**)], but (**3**) rapidly reverts to (**1**) on deprotonation [*via* (**4**)] (Figure 1). In order to examine the structural basis affording such easy sequential transformations, we have undertaken an *X*-ray structural analysis of (**1**) (recrystallized from MeCN). A saucer-like three-dimensional structure is expected for (**1**), because its perimeter is very similar to that of corannulene (**5**).[2] This expectation was confirmed by the structural determination (Figure 2).

The structures of each of the two independent molecules in the asymmetric unit show only slight conformational differences.† The *cis*-difuryl ethene moiety is nearly planar in both conformations, holding the furan oxygens 10.6 and 14.9°

† *Crystal data*: monoclinic. space group $P2_1/n$, $a$ = 16.763(4), $b$ = 11.998(2), $c$ = 12.278(3) Å, β = 106.83(2)°, $Z$ = 8. 4813 Independent reflections were measured in the ω–2θ scan mode in a Rigaku AFC-5 diffractometer, using graphite-monochromated Mo-$K_\alpha$ radiation (λ = 0.7107 Å). 3978 reflections with $F_o \geq 2\sigma(F_o)$ were used in the structure solution by direct methods and full-matrix least-squares refinement; $R$ = 7.6%. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

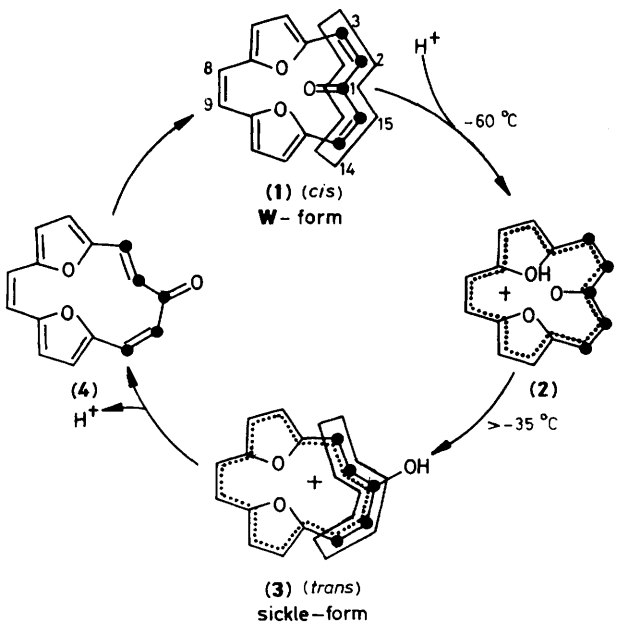


**Figure 1.** [15]Annulenone–hydroxy[15]annulenylium ion cycle.

(5)[2]

upward from the corresponding mean planes of molecules A and B, respectively. The most prominent feature is that each C=O group is inclined at an angle of 57.9° to the mean square plane. This angle is very close to the dihedral angle of cyclo-octatetraene (55.7°).[3] As a consequence, all the bond angles and bond lengths of (**1**) show approximately normal values, and the C(1)–C(2) single and C(2)=C(3) double bond distances are also close to the corresponding values in cyclo-octatetraene (1.462 and 1.334 Å). The structural data for the difuryl ethene moiety shows good agreement with data for the recently prepared [20]annulene tetraoxide,[4] which contains two *cis*-difuryl ethene moieties.

From the crystal data we have made the following observations. (i) The molecule consists of two segments, a planar looped segment encompassing atoms C(4)–C(13), and a non-planar flexible segment formed out of the five $sp^2$ carbon centres C(3)–C(2)–C(1)–C(15)–C(14) in which bond alternation is prominent. In these segments, the mobilities and planarities are very different, and this dual structural feature of (**1**) produces a sequential motion that makes (**1**) fluctuate in conformation.

(ii) The C(1)–C(15) single and C(2)=C(3) double bonds of (**1**) are nearly parallel to each other (Figure 2). On protonation, the bond angle C(15)–C(1)–C(2) is slightly widened to keep the above two bonds parallel. This induces a single rotational motion around the C(1)–C(2) single bond to cause isomerization (**2**) → (**3**). Thus,[1b] the isomerization becomes an extremely fast process such that it can be detected only by using low-temperature n.m.r. spectroscopy. Conversely, on deprotonation, the mono-*trans*-[15]annulenone (**4**) should be destabilized by the presence of the inside hydrogen, and isomerization (**4**) → (**1**) takes place. Consequently, the net result of these two isomerizations is to make a chemical cycle.

(iii) In the presence of $H^+$, the flexible segment of (**1**) can undergo a co-operative $H^+$-binding cycle. The conformational change (**2**) → (**3**) takes place causing better $H^+$-binding, since the annulenyl ion (**3**) can bind to $H^+$ more tightly than (**2**), since (**3**) binds to $H^+$ at the outside of the perimeter to adopt a planar geometry. The segmental motion provides two relationships $\{[(\mathbf{1})]/[(\mathbf{4})] > 1$, $pK_a$ of (**2**) < $pK_a$ of (**3**)$\}$[5] which satisfy two requirements for causing co-operative $H^+$-binding.[6]

(iv) The rigid half of (**1**) keeps both ends of the flexible segment at an almost constant distance, regardless of the *cis*/*trans* geometries and of the protolytic/deprotolytic states. Therefore, either 'bicycle pedal' motion or 'concerted twisting motion on the *n*-th $sp^2$ carbon atom' (CT-*n* mechanism)[7] may become responsible for such rapid isomerizations. We suggest that isomerization (**1**) → (**2**) → (**3**) may be likened to the isomerization sequence $\mathbf{M}_{412}(cis) \rightarrow H^+ \cdot \mathbf{M}_{412}(cis) \rightarrow \mathbf{O}_{640}$ that occurs in the active site of bacteriorhodopsin,[8] although these two chromophores are very different from each other (Figure 3). Indeed, the flexible segment of (**1**) can undergo formally analogous isomerizations (**W** to sickle transformation) that the specific five $sp^2$ atoms of retinylidene Schiff's base [C(12), C(13), C(14), C(15), and the N atom] can undergo in the protein (sickle to **W** transformation), as depicted in Figure 3 (boxed areas).

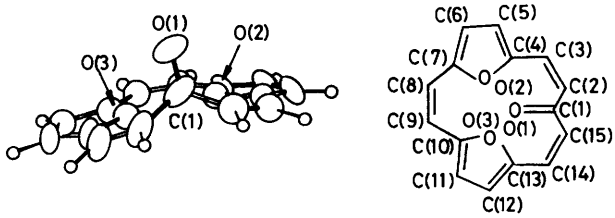


**Figure 2.** Structure of $C_{15}H_{10}O_3$ [(**1**): molecule A]. *Bond lengths*: C(1)–O(1) 1.217(5), C(1)–C(2) 1.484(5), C(2)–C(3) 1.322(6), C(3)–C(4) 1.439(5), C(4)–O(2) 1.383(4), C(4)–C(5) 1.361(6), C(5)–C(6) 1.413(5), C(6)–C(7) 1.371(6), C(7)–O(2) 1.373(4), C(7)–C(8) 1.432(5), C(8)–C(9) 1.351(6), C(9)–C(10) 1.413(6), C(10)–O(3) 1.379(4), C(10)–C(11) 1.382(6), C(11)–C(12) 1.400(6), C(12)–C(13) 1.383(6), C(13)–O(3) 1.372(5), C(13)–C(14) 1.433(5), C(14)–C(15) 1.325(7), C(15)–C(1) 1.484(7) Å. *Bond angles*: O(1)–C(1)–C(2) 122.2(4), C(1)–C(2)–C(3) 127.3(3), C(2)–C(3)–C(4) 128.1(3), C(3)–C(4)–O(2) 116.8(3), C(3)–C(4)–C(5) 133.1(3), O(2)–C(4)–C(5) 109.9(3), C(4)–C(5)–C(6) 107.0(4), C(5)–C(6)–C(7) 106.8(4), C(6)–C(7)–O(2) 109.8(3), C(6)–C(7)–C(8) 129.6(3), O(2)–C(7)–C(8) 120.6(3), C(7)–C(8)–C(9) 134.0(4), C(8)–C(9)–C(10) 132.5(3), C(9)–C(10)–O(3) 121.4(3), C(9)–C(10)–C(11) 129.6(3), O(3)–C(10)–C(11) 109.0(3), C(10)–C(11)–C(12) 107.2(3), C(11)–C(12)–C(13) 107.3(4), C(12)–C(13)–O(3) 109.0(3), C(12)–C(13)–C(14) 133.1(4), O(3)–C(13)–C(14) 117.9(4), C(13)–C(14)–C(15) 127.7(5), C(14)–C(15)–C(1) 127.9(4), C(15)–C(1)–O(1) 122.8(4) C(15)–C(1)–C(2) 115.0(3)°.

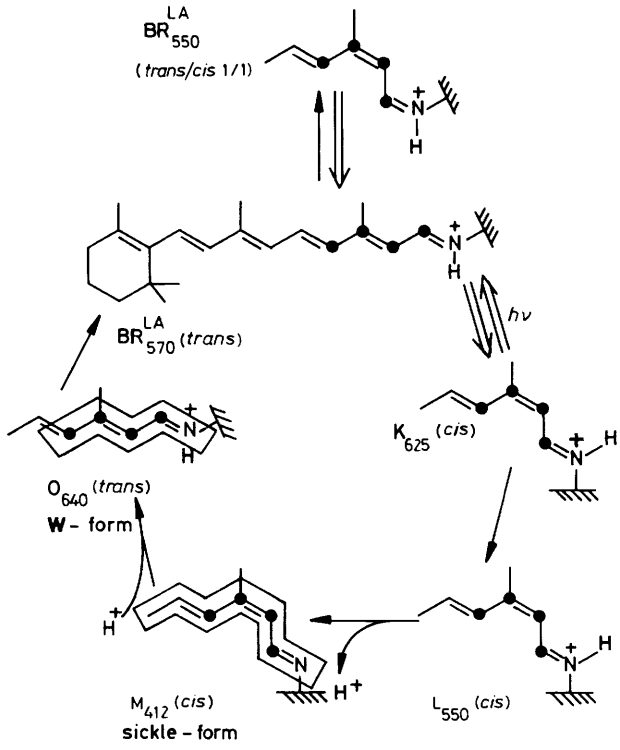


**Figure 3.** The proton pumping cycle of bacteriorhodopsin (BR). LA and DA indicate light- and dark-adapted BR, respectively (according to Prof. K. Nakanishi, 1986, Komaba, Tokyo).[8]

In conclusion, although we have not yet found a rigorous answer to determine what types of motion are really responsible for the isomerization (**1**) → (**3**), we have now obtained a structural basis to understand why (**1**) can drive a co-operative $H^+$-binding cycle with fast isomerization rates.

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