Photochemical Syntheses. XI*  
X-Ray Analysis and Molecular Structure of  
1,8-Diphenyl-1a,2,7,7a-tetrahydro-1,2,7-
metheno-1H-cyclopropa[b]napthalene, a  
Naphthalene–Diphenylacetylene Photoadduct

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Abstract  
The structure of the title compound (1) has been confirmed by X-ray crystal structure analysis.

Under the influence of Pyrex-filtered ultraviolet light naphthalene and diphenyl-
acetylene (tolan) form a photoadduct for which the structure (1) has been proposed  
on spectroscopic and chemical grounds. Additional support for this assignment has  
been found in the intermediacy of (2) in the formation of (1) and in the properties  
of related photoadducts obtained from substituted naphthalenes and from other  
diarylacetylenes. However, to our knowledge the bridged ring system in (1) has so  
far not been obtained by other methods and definitive proof for structure (1) has not  
been available. We have therefore carried out an X-ray crystal structure analysis on  
the naphthalene–diphenylacetylene photoadduct which has confirmed structure (1)  
for this compound.

An outstanding feature of structure (1) is the degree to which the bridgehead atoms  
are distorted from tetrahedral geometry and in Table 1 we list relevant parameters.

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for these atoms as obtained in the present work. While the bond lengths and angles for C1a (or C7a), C2 (or C7) and C8 are consistent with those observed in other three- and four-membered carbocyclic rings the bond angles of C1 are to our knowledge without parallel.

<table>
<thead>
<tr>
<th>Distances (Å)</th>
<th>Angles (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C8-C1 1.59</td>
<td>C2-C2a,C1a 115</td>
</tr>
<tr>
<td>C2 1.55</td>
<td>C2a,C8 106</td>
</tr>
<tr>
<td>C7 1.57</td>
<td>C8,C1a 85</td>
</tr>
<tr>
<td>C1' 1.48</td>
<td>C1a-C2,C1 93</td>
</tr>
<tr>
<td>C1-C1a 1.51</td>
<td>C2,C7a 104</td>
</tr>
<tr>
<td>C7a 1.52</td>
<td>C7a,C1 60</td>
</tr>
<tr>
<td>C1' 1.47</td>
<td>C7a-C1a,C1 59</td>
</tr>
<tr>
<td>C7a-C7 1.51</td>
<td>C7,C1 94</td>
</tr>
<tr>
<td>C1a 1.53</td>
<td>C7,C1a 106</td>
</tr>
<tr>
<td>C1a-C2 1.55</td>
<td>C1-C1a,C1' 136</td>
</tr>
<tr>
<td>C2-C2a 1.48</td>
<td>C1a,C7a 61</td>
</tr>
<tr>
<td>C7-C6a 1.52</td>
<td>C1a,C8 86</td>
</tr>
</tbody>
</table>

The present results confirm earlier estimates of the strain at C1a (or C7a) and C2 (or C7), which were based on measurement of the appropriate $^{13}$C–H coupling constants (c. 180 and 150 Hz, respectively).$^9$

Compound (I), $C_{24}H_{18}$, crystallizes from a mixture of benzene–methanol–light petroleum as thin laths in the monoclinic space group $P2_1/c$ with unit-cell parameters $a = 16.382(10)$ Å, $b = 6.360(3)$ Å, $c = 18.051(11)$ Å, $\beta = 115.6(1)^\circ$; $U = 1695.6$ Å$^3$, $D_x = 1.20$ kg/m$^3$, $Z = 4$. The structure was solved by direct methods with the xray72 system,$^{10}$ and the fractional coordinates and individual isotropic temperature factors of the non-hydrogen atoms refined by least squares procedures to a final $R = 0.097$ for 811 structure magnitudes ($I > 2\sigma(I)$). The intensities were collected from an automatic diffractometer with CuK$\alpha$ radiation. The hydrogen atoms were located by difference Fourier and included in the final refinement cycle, but no parameters were refined.

A full account of this work will be published elsewhere.

Acknowledgment

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