

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]naphthalene, a
Naphthalene-Diphenylacetylene Photoadduct

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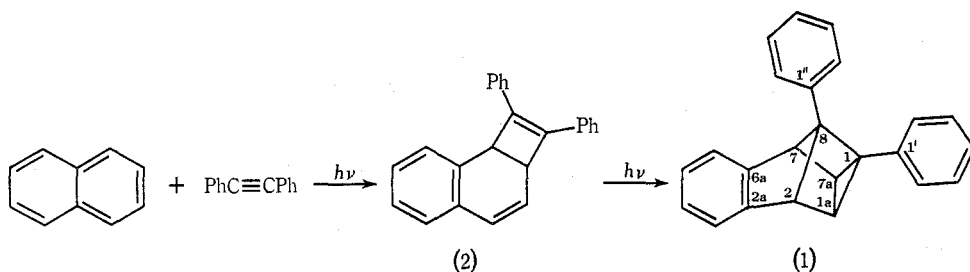
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Abstract

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 diphenylacetylene (tolan) form a photoadduct for which the structure (1) has been proposed on spectroscopic and chemical grounds.¹ Additional support for this assignment has been found in the intermediacy of (2) in the formation of (1),²⁻⁵ and in the properties of related photoadducts obtained from substituted naphthalenes^{6,7} and from other diarylacetylenes.⁸ 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

* Part X, *Aust. J. Chem.*, 1976, 29, 1783.

¹ Sasse, W. H. F., Collin, P. J., and Sugowdz, G., *Tetrahedron Lett.*, 1965, 3373.

² Collin, P. J., and Sasse, W. H. F., *Tetrahedron Lett.*, 1968, 1689.

³ Collin, P. J., and Sasse, W. H. F., *Aust. J. Chem.*, 1971, 24, 2325.

⁴ Teitei, T., Wells, D., and Sasse, W. H. F., *Aust. J. Chem.*, 1973, 26, 2129.

⁵ Teitei, T., Wells, D., and Sasse, W. H. F., *Aust. J. Chem.*, 1975, 28, 571.

⁶ Sasse, W. H. F., Collin, P. J., Roberts, D. B., and Sugowdz, G., *Aust. J. Chem.*, 1971, 24, 2151.

⁷ Sasse, W. H. F., Collin, P. J., Roberts, D. B., and Sugowdz, G., *Aust. J. Chem.*, 1971, 24, 2339.

⁸ Teitei, T., Collin, P. J., and Sasse, W. H. F., *Aust. J. Chem.*, 1972, 25, 171.

for these atoms as obtained in the present work. While the bond lengths and angles for C 1a (or C 7a), C 2 (or C 7) and C 8 are consistent with those observed in other three- and four-membered carbocyclic rings the bond angles of C 1 are to our knowledge without parallel.

Table 1 Interatomic distances and angles for the title compound (1)

Distances (Å)		Angles (degrees)	
C 8-C 1	1.59	C 2-C 2a, C 1a	115
C 2	1.55	C 2a, C 8	106
C 7	1.57	C 8, C 1a	85
C 1''	1.48	C 1a-C 2, C 1	93
C 1-C 1a	1.51	C 2, C 7a	104
C 7a	1.52	C 7a, C 1	60
C 1'	1.47	C 7a-C 1a, C 1	59
C 7a-C 7	1.51	C 7, C 1	94
C 1a	1.53	C 7, C 1a	106
C 1a-C 2	1.55	C 1-C 1a, C 1'	136
C 2-C 2a	1.48	C 1a, C 7a	61
C 7-C 6a	1.52	C 1a, C 8	86
		C 1-C 7a, C 1'	132
		C 7a, C 8	85
		C 8, C 1'	132
		C 8-C 2, C 1	90
		C 2, C 7	95
		C 2, C 1''	121
		C 1, C 1''	126
		C 1, C 7	89
		C 7, C 1''	126
		C 7-C 2a, C 8	104
		C 6a, C 7a	114
		C 7a, C 8	86

The present results confirm earlier estimates of the strain at C 1a (or C 7a) and C 2 (or C 7), which were based on measurement of the appropriate ^{13}C -H coupling constants (*c.* 180 and 150 Hz, respectively).⁹

Compound (1), $\text{C}_{24}\text{H}_{18}$, crystallizes from a mixture of benzene-methanol-light petroleum as thin laths in the monoclinic space group $P2_1/c$ with unit-cell parameters $a = 16.382(10)$, $b = 6.360(3)$, $c = 18.051(11)$ Å, $\beta = 115.6^\circ(1)$; $U = 1695.6$ Å³, $D_x = 1.20$ kg/m³, $Z = 4$. 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 ($I \geq 2\sigma_I$). The intensities were collected from an automatic diffractometer with Cu K α 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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⁹ Collin, P. J., *Aust. J. Chem.*, 1972, **25**, 425.

¹⁰ Stewart, J. M., Kruger, G. J., Ammon, H. L., Dickinson, C., and Hall, S. R., The XRAY System—Version of June 1972, Technical Report TR-192 of the Computer Science Center, University of Maryland (1972).