

4,14-DIVINYL-(E,E)-[4.4]PARACYCLOPHANE-1,11-DIENE. AN UNUSUAL
PRODUCT FROM A 1,10-HOFMANN ELIMINATION

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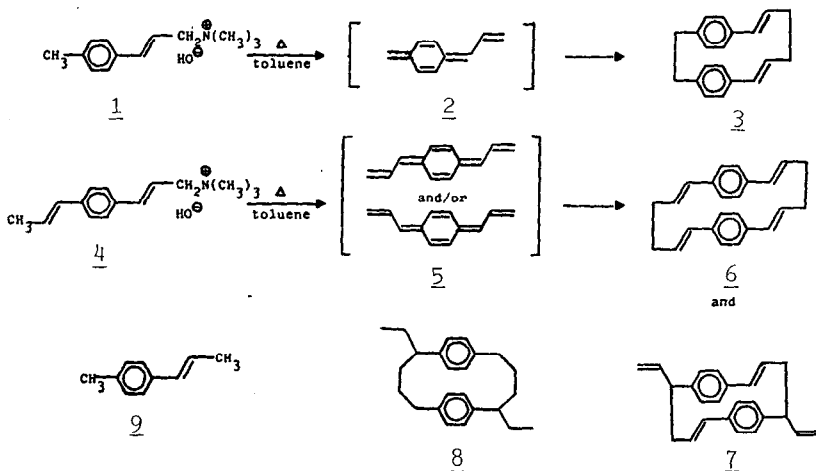
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Summary: The isolation of 4,14-divinyl-(E,E)-[4.4]paracyclophane-1,11-diene from the cyclodimerization reaction of 7,8-divinyl-p-quinodimethane and its characterization are described. The title compound features head-to-tail, cofacially paired styryl moieties and its UV spectrum is compared in terms of electronic and structural characteristics with that of its head-to-head analogue and an open chain model compound.

Extended 1,x-eliminations of the Hofmann type where $x = 8$ or 10 (Scheme 1) have proved useful for the preparation of the styryl^{1,2} (3) and divinylbenzene³ (6) analogues of [2.2]paracyclophane. Whereas similar, more conventionally prepared cyclophanes containing cis unsaturation in the alkyl bridges are less strained, more conformationally mobile and relatively lacking in transannular interactions⁴, the trans configuration of double bonds in 3 and 6 provide the correct molecular geometry to produce tightly held, interactive, cofacial vinyl aromatic moieties. Such compounds have recently found application in intra-intermolecular cyclopolymerization reactions to give structurally unique polymers containing bridged aromatic rings² and are of general interest for studying electronic interactions between vinyl-aromatics at close spatial orientations. We report here the isolation and characterization of a second, unusual dimer from the 1,10-elimination of 4 which features head-to-tail paired styryl moieties; 4,14-divinyl-(E,E)-[4.4]paracyclophane-1,11-diene (7).

Dimer 6 was isolated (30%) from the ether extracts (Soxhlet) of the residue from the pyrolysis of 4 as previously described³; by reduction, filtration and recrystallization from CHCl_3 . Concentration of the liquors from the isolation of 6, followed by column chromatography (petroleum ether on silica gel) gave 7, the product of head-to-tail [8+8] cyclodimerization of 7,8-divinyl-p-quinodimethane (5), as the major fraction in notably high yield (13%); mp (MeOH) 136.0-137.0° (sealed capillary, melts with apparent polymerization). Anal. Calcd for $\text{C}_{24}\text{H}_{24}$: C, 92.26; H, 7.74. Found: C, 92.28; H, 7.71. IR(KBr): ca. 965 and 915 cm^{-1} , strong. MS: m/e 312(M^+ , 11%), 156(100), 141(42), 128(37), 115(89). ¹H-NMR (360 MHz, CDCl_3): δ 7.1-6.9(2H, m), 6.9-6.6(6H, m), 6.5-6.1(2H, m), 5.5-5.0(8H, m), 3.8-3.4(2H, m), 2.9-2.2(4H, m). The elemental and



mass spectral analyses confirm 7 as being an isomer of 6, the mass spectra of both compounds being nearly identical³. The strong IR bands at 915 and 965 cm^{-1} indicate, respectively, the presence of both vinyl and trans double bonds. The $^1\text{H-NMR}$ spectrum of 7 is complex but consistent with the proposed structure⁵.

Catalytic (Pd/C) hydrogenation of 7 gave 1,11-diethyl-[4.4]paracyclophane (8) in 69% yield after recrystallization; mp (EtOH/ H_2O) 113.5–114.5 $^\circ$. Elemental⁶ and mass spectral⁶ analyses of 8 confirm the addition of 8 hydrogens; consistent with 4 double bonds in 7, while the IR spectrum lacks bands at 915 and 965 cm^{-1} as expected. The $^1\text{H-NMR}$ spectrum⁶ of 8 shows, by integration of methyl triplets, that 2 ethyl groups are present; confirming that 7 has 2 vinyl groups. The two closely spaced methyl triplets also suggest that 7 is formed as a mixture of geometric isomers.

The fixed and opposing geometry of styryl groups in 3 and 7 may serve as good model systems for the study of electronic interactions between styryl compounds as dependent on spatial orientation. Ultraviolet spectroscopy has long been used for qualitative investigation of transannular electronic interactions in cyclophanes and can often provide useful structural information^{7,8}. The UV spectra for 3, 7 and model compound 9 are shown in Figure 1. At first glance the spectra of 3 and 7 appear quite similar and both exhibit a broadening of bands and loss of fine structure, relative to 9, which is typical of "tight" cyclophane structures⁷. Also apparent are considerable bathochromic shifts of the longest wavelength bands for 3 and 7, relative to 9. Such shifts in p-cyclophanes have been interpreted as being due, at least partially, to transannular electronic interactions⁷. The absorption bands for 3 at long wavelengths (>295 nm) are more distinct, bathochromically shifted and tail out with more intensity to longer wavelengths than for 7. This suggests that, even though the intensity of the π to π^* transition at ca. 250 nm is stronger in 7 due to structural characteristics discussed below, transannular

electronic effects are somewhat more pronounced in 3, perhaps resulting from more favorable π -molecular orbital interactions due to geometry.

Useful structural information can be obtained from the intensity maxima of the π to π^* transition for 3, 7 and 9 at 252, 256 and 253 nm, respectively. Calculation of the effective interplanar angle θ between the trans double bond and phenyl rings in 3 and 7 using Braudes' treatment^{4,9} leads to θ values of 35° and 4° , respectively.

These values are in qualitative agreement with θ values estimated

from molecular models. These model studies suggest that the phenyl rings and trans double bonds in 7 are relatively planar, likely due to steric interaction of the phenyl/double bond linkage with the opposing phenyl ring. This interaction is absent in 3 and the molecule may relieve ring strain by twisting about the phenyl/double bond linkage.

These observations are also consistent with the small hypsochromic and bathochromic shifts in λ_{max} for the π to π^* transition in 3 and 7 compared to 9. Since the phenyl/double bond linkage should develop more double bond character in the excited state, the twisted linkage in 3 is expected to raise the energy of the π to π^* transition somewhat, resulting in the small hypsochromic shift observed¹⁰. Conversely, models indicate that some strain in 7 is relieved by twisting about the trans double bonds. As these double bonds should have more single bond character in the excited state, lessening the resistance to twisting, the energy of the transition should be lowered, leading to the small bathochromic shift observed¹⁰.

Although the UV spectra of 3, 7 and 9 yield qualitative information about the structure and distribution of strain in the molecules, they give no information about the exact geometry of 3 and 7 with respect to the orientation of trans double bonds relative to one another or whether the molecules are conformationally mobile. More exact studies and more sensitive methods (photoelectron spectroscopy, fluorescence) are also needed to clarify the nature of differences in through-space electronic interactions in 3 and 7.

The isolation of 7 from the 1,10-Hofmann elimination of 4 is also of mechanistic interest. Although several publications have appeared on the generation and reactions of vinyl-p-quinodimethane type species^{1,3,11,12}, the factors that govern their cycloaddition behavior are not well understood. In particular, although several cyclophanes containing 4-carbon bridges have been ob-

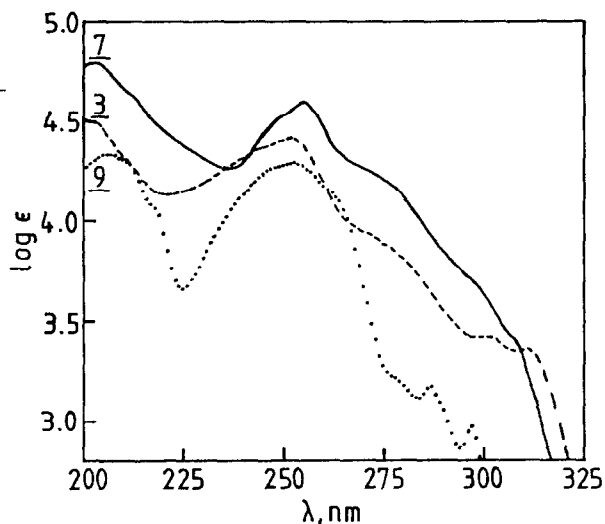


Figure 1 UV absorbance spectra of 3, 7 and 9 (cyclohexane).

tained from such reactions^{11,12}, all have been reported to contain cis unsaturation in the bridges. To our knowledge, 7 is the first isolated example of head-to-tail dimer formation from such cycloaddition reactions which contains the more strained trans unsaturation in the alkyl bridges. Elucidation of the factors controlling such cycloaddition reactions may help expand the scope of their synthetic utility.

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References and Notes

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4. D. J. Cram and K. C. Dewhirst, *J. Am. Chem. Soc.*, **81**, 5963 (1959).
5. The NMR spectrum of 7 exhibits shielding effects relative to 3² and 9⁸ consistent with a tight cyclophane structure but with some decrease in total cofacial π -system overlap compared to 3. Further deshielding of 2 protons in 7 at ca. δ 7.0 is consistent with molecular models that suggest 2 aromatic protons lack substantial overlap with the shielding zone of the opposing trans double bonds. Comparison of the spectrum of 7 with that of 3² and the spectrum of 8⁶ with that of [6.2]paracyclophane⁻ (Ref. 1) eliminates the possibility of 7 being the product of head-to-head [8+8] cyclo-dimerization of 5.
6. Compd 8, Anal. Calcd for C₂₄H₃₂: C, 89.94; H, 10.06. Found: C, 90.05; H, 10.07. MS: m/e 320(M⁺, 26%), 291(18), 221(14), 171(24), 145(18), 131(100), 117(96), 105(78), 91(69). ¹H-NMR (360 MHz, CDCl₃): δ 6.67(8H, m), 2.6-1.1 (18H, m, m), 0.77(6H, two close triplets).
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8. In the following discussion it is assumed that the vinyl double bonds in 7 act as isolated chromophores and do not exhibit any influence in the spectral range studied (see Ref. 10, p 30). Model compound 9 was made by reaction of p-tolualdehyde with ethylmagnesiumbromide in diethyl ether (dilute HCl workup), followed by dehydration with phosphorous pentoxide in refluxing benzene and distillation twice under reduced pressure. IR(NaCl plates): 965 cm⁻¹, strong. ¹H-NMR(80 MHz, CDCl₃): δ 7.11(4H, q, AB, J = 8 Hz), 6.5-5.75(2H, m), 2.26(3H, s), 1.82(3H, d, J = 5 Hz).
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