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DEHYDRO-*ANTI*-4,5,15,16-TETRAMETHYL[2_2](5,8)PHENALENOPHANE-1,12-DIENE

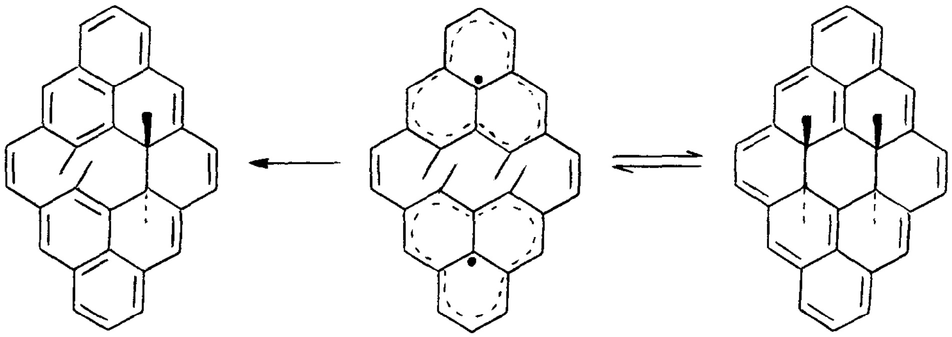
W. D. Rohrbach and V. Boekelheide*
Department of Chemistry, University of Oregon, Eugene, Oregon 97403

and

A. W. Hanson
Atlantic Research Laboratory, National Research Council of Canada
Halifax, N. S., Canada B3H 3Z1

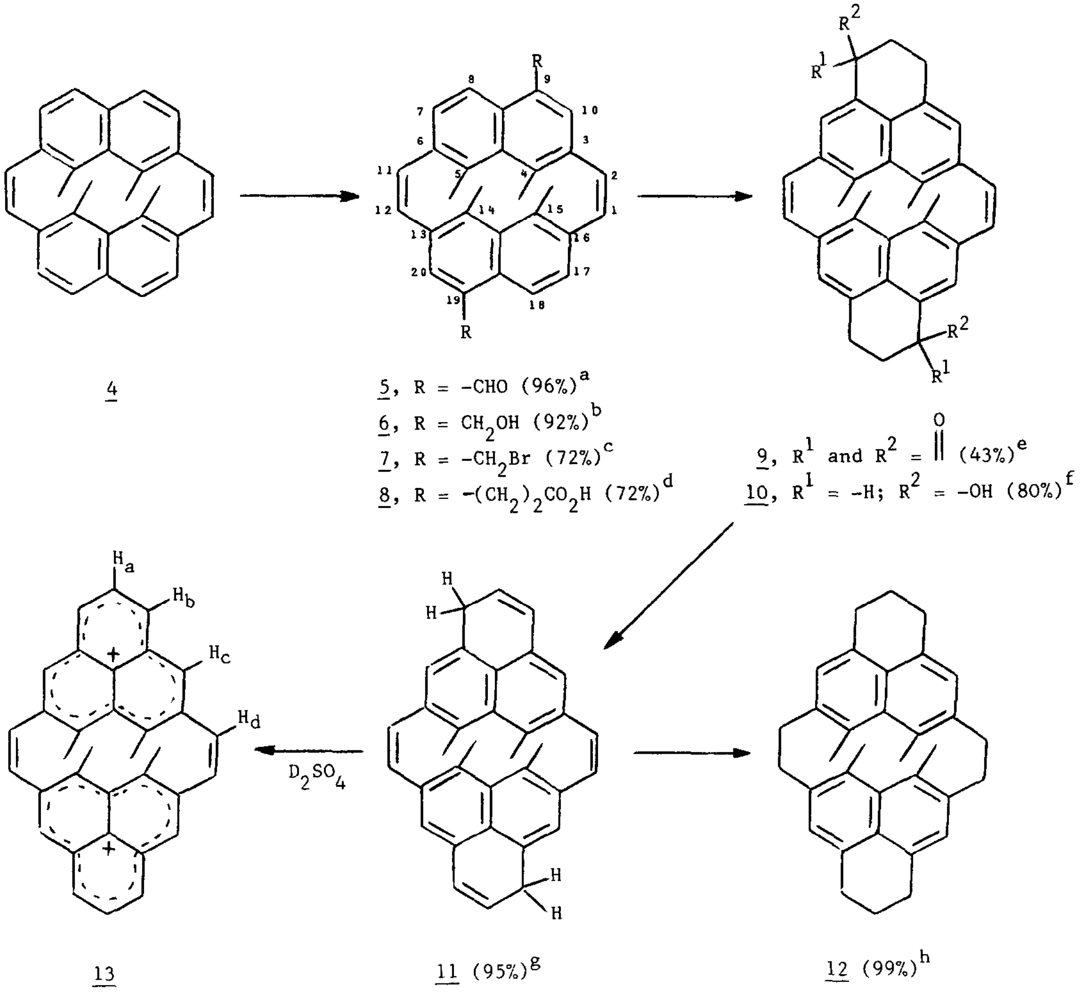
Abstract: A synthesis of *anti*-4,5,15,16-tetramethyl[2_2](5,8)phenalenophane-1,12-diene (11) is described as well as its transformation via a radical abstraction process to an enantiomeric mixture of the Cope rearrangement product 3.

The interaction through space of diradicals held rigidly in cage structures is of current interest.[1,2] Because of the exceptional stability of the phenalene radical, Murata has pursued this goal by synthesizing diphenalenes.[3,4] It would appear that the ideal molecule for this purpose, though, would be a cyclophane having two phenalene radical moieties held rigidly face-to-face at a short distance. Although a synthesis of this ideal molecule seems forbiddingly difficult, a related molecule of interest and somewhat easier to synthesize is dehydro-4,5,15,16-tetramethyl[2_2](5,8)phenalenophane-1,12-diene (1). It was anticipated that 1 might undergo valence tautomerization to 2, a behavior encountered with analogous molecules,[5,6] but tautomerization to 2 would give a rigid [22]annulene, a molecule of high interest in its own right.



3 1 2

Our synthesis of *anti*-4,5,15,16-tetramethyl[2_2](5,8)phenalenophane-1,12-diene (11) is outlined below. The preparation of the starting material, *anti*-4,5,14,15-tetramethyl[2_2](2,7)-naphthalenophane-1,11-diene (4) is described elsewhere.[7] The steps in the transformation of 4 to 11 involved the standard elaboration of a naphthalene moiety to a phenalene, but carried out simultaneously in two separate regions of the molecule. This led to isomeric mixtures. For example, formylation of 4 gave both the 9,18- and 9,19-diformyl derivatives in roughly equal amounts. These mixtures were then carried through each of the subsequent steps with full characterization but without separation, since attempts at separation of these mixtures proved to be exceedingly difficult and since both isomers eventually lead to the same final product. To save space only one of the isomers at each stage is shown in the synthetic scheme.



4

5, R = -CHO (96%)[a]
6, R = CH_2OH (92%)[b]
7, R = $-CH_2Br$ (72%)[c]
8, R = $-(CH_2)_2CO_2H$ (72%)[d]

9, R^1 and R^2 = $\overset{O}{\|}$ (43%)[e]
10, R^1 = -H; R^2 = -OH (80%)[f]

13

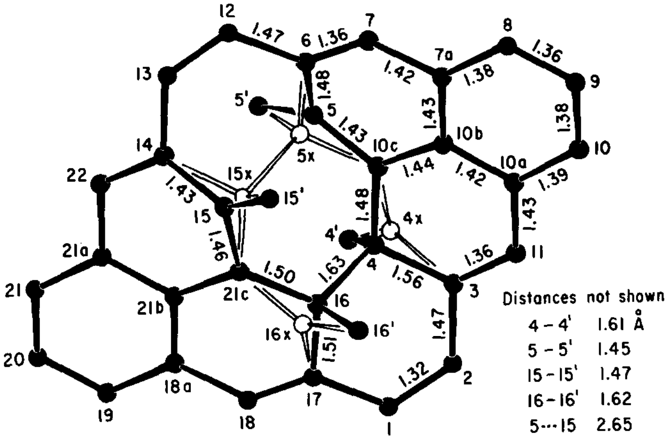
11 (95%)[g]

12 (99%)[h]

[a] Cl_2CHOMe, $SnCl_4$, CH_2Cl_2; [b] $LiAlH_4$, THF; [c] PBr_3, CH_2Cl_2; [d] (1) NaOEt, $CH_2(CO_2Et)_2$, EtOH; (2) KOH, MeOH, then HCl; (3) sublime at 200°C; [e] HF; [f] $LiAlH_4$, THF; [g] p-$CH_3C_6H_4SO_3H$, C_6H_6; [h] H_2, Pt, EtOAc

Evidence that 11, as a mixture of isomers, had the correct carbon skeleton was obtained by its clean hydrogenation to 12 to give a single isomer identical in all respects to a known sample.[9] A solution of 11 in deuteriosulfuric acid was deep red and showed only four signals in the aromatic region of its ^{1}H NMR spectrum (δ 7.60 (4 H, s, H_d), 8.57 (2 H, bs, H_a), 9.12 (4 H, s, H_c), 9.28 (4 H, s, H_b)) as would be expected for 13. All attempts to prepare a dianion from 11 were unsuccessful and reaction of 11 with n-butyllithium led to the introduction of n-butyl groups, presumably by electron transfer followed by radical coupling. However, treatment of 11 with triphenylmethyl radical in benzene gave yellow orange needles (34%), mp 264-266°C, having the correct composition and molecular weight for the desired dehydro product. Unexpectedly, though, neither the ultraviolet nor the ^{1}H NMR spectrum of this product was in accord with either of the anticipated structures 1 or 2.[10]

As shown in Figure 1, X-ray crystallographic analysis showed the dehydro product to be an enantiomeric mixture corresponding to 3. Thus, the low energy valence tautomer of 1 is 3 and not 2. The two enantiomers of 3 correspond to two equivalent internal Cope rearrangement isomers. Although the room temperature ^{1}H NMR spectrum of 3 is completely symmetrical,[10] variable temperature ^{1}H NMR studies show the presence of a dynamic equilibrium with the energy barrier for the Cope rearrangement being 9.0 $\pm$ 1.0 kcal/mol.[11]



Distances not shown

4 - 4'	1.61 Å
5 - 5'	1.45
15 - 15'	1.47
16 - 16'	1.62
5···15	2.65

Figure 1. Two enantiomers of 3 occupying a single site (open circles represent atoms belonging to only one enantiomer; solid circles represent atoms belonging to the other, or both).

The crystal structure is four-fold disordered. A molecular site (of nominal symmetry $\bar{1}$) can be occupied by 3, or by its inversion-related enantiomer, or by either of these rotated by (approximately) 180° about 9...20. The occupancy ratios are estimated to be 0.418 each for the enantiomers shown above, and 0.082 for the other two. The distances shown are reasonably consistent with the bond lengths expected for 3. However, they necessarily involve electron-density peaks which result from the superpositon of two or four fractional atoms and may not, therefore, correctly represent individual bond lengths.

The refinement of an ordered, centrosymmetrical hybrid molecule, resembling the superposition shown above, converged at R = 0.10, and there were substantial anomalous peaks in the map of residual electron density. When these were modelled as the resolved portion of an alternatively oriented molecule (180° rotation about 9...20) the refinement converged at R = 0.038. However, the electron-density peaks corresponding to atoms 4 and 5 were unreasonably elongated, suggesting that they should be modelled as two-center structures. This did not change the R index, but the apparent thermal motion of the contributing fractions (4, 4x, 5, 5x) became quite small, and nearly isotropic. The final separations were: 4 - 4x, 0.51(1)Å; 5 - 5x, 0.52(1)Å. A repetition of the analysis with data measured at -150°C led to essentially the same result (4 - 4x = 0.50(1)Å; 5 - 5x(1)Å). We conclude that the peak elongation results from disorder, and not thermal motion. We are unable to say whether the disorder is static ("frozen") or dynamic (such as would result from an ongoing Cope rearrangement).[12]

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References and Notes

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8. The composition and molecular weights of each of the new compounds were established by elemental analysis and/or mass spectrometry. Ultraviolet, infrared, and NMR spectra data are in accord with the assigned structures and are given in ref. 9.
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10. ^{1}H NMR ($CDCl_3$) at room temperature, δ 1.50 (12 H, s, CH_3), 6.43 (4 H, s, -CH=), 7.01 (4 H, s), 7.17 (2 H, m), 7.25 (2 H, s), 7.27(2 H, s); UV (cyclohexane) λ_{max} 445 nm (ε 2060), 331 (10,800), 294 (16,500), 270 (16,500), 232 (21,100); mass spectrum m/e 434,374.
11. A variable temperature ^{1}H NMR study of a solution of *3* in CD_2Cl_2 was made over the temperature range of 25° to -100°C using a Nicolet 360 MHz instrument. We thank Dr. C. E. Klopfenstein for his assistance in this study.
12. Crystal and intensity data were measured with a Picker four-circle diffractometer using θ-2θ scans. At T = 24°C, with Ni-filtered CuK_α radiation, 1161 reflections were observed ($I \geq 3\sigma$) of 1862 scanned ($2\theta < 130°$). At T = -150°C, with graphite-monochromatized MoK_α radiation, 1080 reflections were observed, of 2485 scanned ($2\theta < 55°$). Refinement was by block-diagonal least squares, with final R values of 0.038 and 0.049 for the higher and lower temperatures, respectively. The crystal data and atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK. Any request should be accompanied by the full literature citation for this communication. Supplementary data available: carbon-carbon distances not given in Fig. 1; a list of observed and calculated structure factors. See Announcement to Authors, *Tetrahedron Lett.* *24*, 5154 (1983).

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