Tetrahedron Letters No. 37, pp 3239 - 3240, 1977. Pergamon Press. Printed in Great Britain.

# 1,5-METHANO[10]ANNULENE
# (BICYCLO[5.3.1]UNDECA-1,3,5,7,9-PENTAENE)

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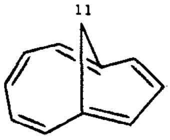
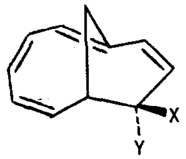
(Received in USA 6 June 1977; received in UK for publication 25 July 1977)

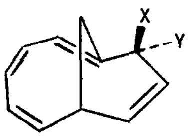
Further to our recent report on the construction of the 1,5-methano[10]annulene ring system, we wish to record the first synthesis and important physical properties of the crystalline parent hydrocarbon (1). Reduction of the known ketone 2[1] with diisobutylaluminum hydride at -70°C led stereospecifically to the *endo*-hydroxy compound 3 which was subsequently treated with two equivalents of triphenylphosphine, benzoic acid, and diethyl azodicarboxylate at 0°C overnight.[2] Separation of the resulting isomeric benzoates 4 and 5 by silica gel column chromatography followed by alkaline hydrolysis afforded the corresponding alcohols, 6 and 7. The stereochemistry of the hydroxy or benzoxy groups of 3, 4, 5, and 6 rests upon the manner of formation and the NMR spectra of these compounds (see Table). Treatment of alcohol 6 with *p*-nitrophenylisocyanate yielded the corresponding urethane 8 which underwent pyrolytic elimination at 300°C to give 1 in *ca*. 20% yield. Silica gel (deactivated) chromatography provided orange, crystalline 1.[3] The CMR spectrum of 1 exhibits only 7 signals even at low temperature (-80°C) and the molecule therefore possesses two fold symmetry, at least on the NMR time scale. Appearance of the high field H signals due to C(11)-$H_{a,b}$ and those in the aromatic region leads to the interpretation that a diamagnetic ring current is induced in this monocyclic 10π-electron system. In contrast to its 1,6-methano counterpart, the electronic absorption of 1 extends deeply into the visible region, an observation reminiscent of the comparison between naphthalene and azulene (see Fig. 1). We intend to evaluate in depth the electronic structure of 1 when an X-ray analysis has been completed.[4]



1.



2. XY = O
4. X = OBz, Y = H
8. X = $O_2CNHC_6H_4NO_2$
3. X = H, Y = OH
6. X = OH, Y = H



5. X = OBz, Y = H
7. X = OH, Y = H

Table 1. Spectral Properties of Compounds[a]

1. CMR (acetone-$d_6$) : $\delta$ 34.7 (t),[b] 125.13 (d), 128.70 (d, C-4 or -9), 130.41 (d, C-9 or -4), 133.51 (d), 144.59 (d), 161.16 (s).
3. PMR : $\delta$ 2.05 (br d, J=12.0 Hz, 1, H-11), 2.38 (s, 1, OH), 3.10 (ddd, J=12.0 Hz, J=4.0 Hz, J=2.0 Hz, 1, H-11), 3.40 (m, 1, H-7), 4.65 (m, 1, H-8), 5.26 (dd, J=10.0 Hz, J=2.0 Hz, 1, H-9), 6.00 (m, 5), 6.44 (br d, J=10.0 Hz, 1, H-10); CMR : $\delta$ 31.2 (dd, C-11), 42.2 (d, C-7), 72.3 (d, C-8), 122.5 (d), 126.8 (d), 127.2 (d), 128.6 (d), 129.4 (d), 131.0 (d), 131.6 (d), 141.2 (s, C-1).
4. PMR : $\delta$ 2.26 (br dd, J=12.0 Hz, J=4.0 Hz, 1, H-11), 3.16 (m, 2), 5.52 (m, 2), 5.96 (m, 5), 6.70 (d, J=10.0 Hz, 1, H-10), 7.47 (m, 3), 8.07 (m, 2).
5. PMR : $\delta$ 2.40 (dd, J=12.0 Hz, J=4.0 Hz, 1, H-11), 3.00 (d, J=12.0 Hz, 1, H-11), 3.45 (m, 1, H-7), 6.00 (m, 8), 7.45 (m, 3), 8.06 (m, 2).
6. PMR : $\delta$ 2.14 (m, 2), 3.08 (m, 2), 4.10 (d, J=4.0 Hz, 1, H-8), 5.48 (dd, J=10.0 Hz, J=4.0 Hz, 1, H-9), 5.92 (m, 5), 6.55 (d, J=10.0 Hz, 1, H-10); CMR : $\delta$ 26.4 (t, C-11), 46.1 (d, C-7), 72.4 (d, C-8), 123.1 (d), 124.0 (d), 126.6 (d), 128.3 (d), 129.4 (d), 132.3 (d), 134.0 (d), 141.1 (s, C-1).
7. PMR : $\delta$ 2.34 (m, 2), 2.88 (br d, J=12.0 Hz, 1, H-11), 3.37 (m, 1, H-7), 4.44 (dd, J=2.5 Hz, J=1.5 Hz, 1, H-10), 5.90 (m, 7); CMR : $\delta$ 26.4 (t, C-11), 43.7 (d, C-7), 71.2 (d, C-10), 122.2 (d), 123.3 (d), 127.0 (d), 127.8 (d), 131.9 (d), 135.4 (d), 135.7 (d), 146.6 (s, C-1).

[a] NMR spectra use Me$_4$Si as reference and CDCl$_3$ as solvent, unless otherwise specified. All compounds gave parent ions of satisfactory accurate mass (MS-50). [b] Multiplicity in off-resonance spectra.

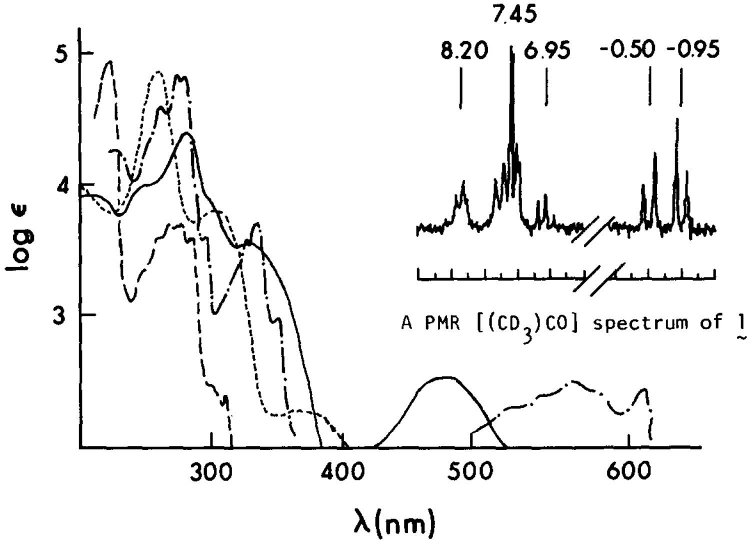


Fig. 1. Uv spectra (cyclohexane) of 1 (——), 1,6-methano[10]annulene(----), naphthalene (— —), and azulene (—·—).

### References and Notes

1. S. Masamune, D. W. Brooks, K. Morio, and R. L. Sobczak, J. Am. Chem. Soc., 98, 8277 (1976). The presence of 1 in a crude mixture was assured previously (GLC-mass), but mainly because of technical problems involved in isolation we were unable to obtain 1 until the present procedure was developed.
2. A. K. Bose, B. Lal, W. A. Hoffman III, and M. S. Manhas, Tetrahedron Letters, 1619 (1973).
3. Because of thermal instability of 1 no attempt was made to measure its melting point.
4. We thank the National Research Council of Canada for financial support.