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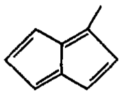
1-Methylpentalene[1]

Sir:

Over the past years there have been many attempts to synthesize the hydrocarbon pentalene.[2] Up to the present success has attended on the preparation of aromatic derivatives[3,4] or the dianion[5] only. *In absentia* pentalene has been the subject of numerous calculations both in the ground state[6] and in the excited state,[7,8] the bond lengths being considered both as equal (symmetric) or unequal.

We wish to report experiments which lead us to believe that we have achieved the synthesis of 1-methylpentalene (**1**). It seemed likely, in view of the lack of success up to the present, that the object should be to generate pentalene in the absence of potential nucleo- or electrophiles. The retro-Diels–Alder was chosen as the generative step. Addition of 4-bromo-3-buten-2-one[9] to cyclopentadiene gave the adduct, which was then treated with the sodium salt of cyclopentadiene to give **2** in 51% yield. This was treated without purification with methylamine in methanol to give a mixture of two isomers. The major isomer **3** (80%) [*Anal.* Calcd for $C_{14}H_{14}$: C, 92.26; H, 7.74. Found: C, 92.44; H, 7.82; λ_{max} 377, 278 nm (ϵ 620, 11,000)] was clearly a fulvene, and the 100-MHz nmr spectrum indicated the contiguity of the fulvene vinyl protons and the continuing presence of the methyl group. The mass spectrum confirmed the molecular weight (*m/e* 182) and, in addition, gave us encouragement since the base peak (*m/e* 116) indicated the loss of cyclopentadiene, *i.e.*, the formation of the **1** cation.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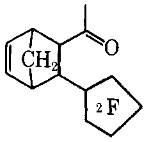

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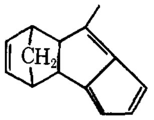

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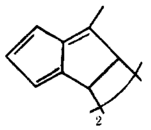

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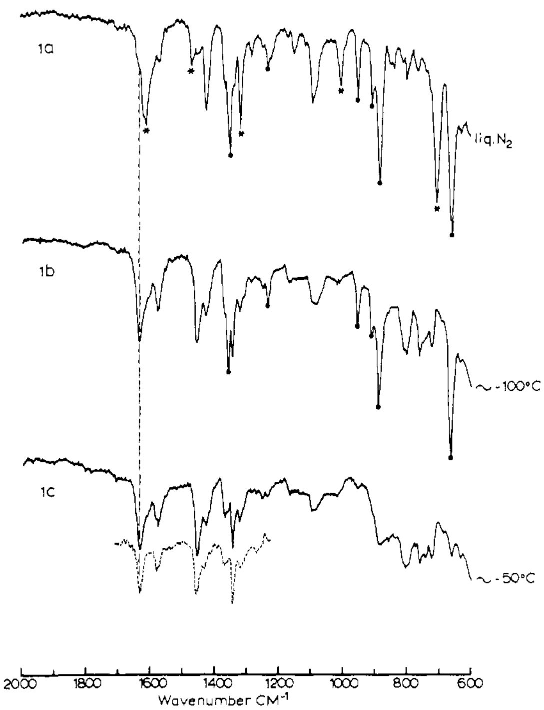

Figure 1. Infrared spectra of thermolysate of **3**: (a) at −196°; (b) at ∼−100°; (c) at ∼−50°; • bands assigned to cyclopentadiene; * bands assigned to **1**.

Thermolysis of **3** at 600° ($<5\ \mu$)[10,11] gave a crude product consisting essentially of cyclopentadiene and a mixture of two isomers. One of these has been obtained in crystalline form, mp 135–136° dec (pentane) [*Anal.* Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 93.30; H, 6.89; λ_{max} 387, 262 nm (ϵ 1400, 26,300)], and is assigned the structure **4** (or geometrical isomer). The molecular weight was confirmed mass spectrometrically, and the much more intense base peak was that for the methylpentalene cation (or isomer). The absorption spectrum of **4** indicates the presence of two fulvene moieties. The nmr spectrum[12] fully confirmed the gross structure. The circumstantial evidence that **1** had been generated by the retro-Diels–Alder reaction on **3** seemed strong. Further, more direct evidence was obtained as follows.

Flash thermolysis of **3** and condensation in a cryostat at −196° on a sodium chloride plate[13] gave the spectrum indicated in Figure 1a. This we believe to be the spectrum of **1** together with that of cyclopentadiene and a small amount of **3** or **4**. At −100° (Figure 1b) the bands attributed to **1** disappear and are replaced by those of **4**. At −50° (Figure 1c) the cyclopentadiene

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(1) Flash Thermolysis. VI. For part V see R. A. Marty and P. de Mayo, *Chem. Commun.*, 127 (1971).

(2) See, *inter alia*, E. D. Bergmann in "Non-benzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience, New York, N. Y., 1959; G. M. Badger in "Aromatic Character and Aromaticity," Cambridge University Press, New York, N. Y., 1969. The substance appeared on the end papers of the first two editions of Cram and Hammond, but although not synthesized did not achieve the third edition.

(3) C. T. Blood and R. P. Linstead, *J. Chem. Soc.*, 2263 (1952).

(4) E. Le Goff, *J. Amer. Chem. Soc.*, **84**, 3975 (1962).

(5) T. J. Katz, M. Rosenberger, and R. K. O'Hara, *ibid.*, **86**, 249 (1964).

(6) *Inter alia* B. A. Hess and L. J. Schaad, *ibid.*, **93**, 305 (1971); M. J. S. Dewar, *Chem. Soc. Spec. Publ.*, **No. 21**, 177 (1967).

(7) T. Nakajima, Y. Yaguchi, R. Kaeriyama, and Y. Nemoto, *Bull. Chem. Soc., Jap.*, **37**, 272 (1964).

(8) N. C. Baird and R. M. West, *J. Amer. Chem. Soc.*, **93**, 3072 (1971). Modified PPP calculations predict bands at 659 nm (forbidden), 335 nm (f = 0.45), 273 nm (f = 0.29), and 232 (f = 0).

(9) V. D. Nemirovskii, L. F. Chelpanova, and A. A. Petrov, *J. Gen. Chem. USSR*, **31**, 2380 (1961).

(10) J. F. King, P. de Mayo, C. L. McIntosh, K. Piers, and D. J. H. Smith, *Can. J. Chem.*, **48**, 3704 (1970).

(11) E. Hedaya, *Accounts Chem. Res.*, **2**, 267 (1969).

(12) It indicated the symmetry, the presence of the methyl groups, and, by double-irradiation, the proton sequence. We are very much indebted to Dr. M. Gordon for these determinations.

(13) The apparatus will be described in the full paper.

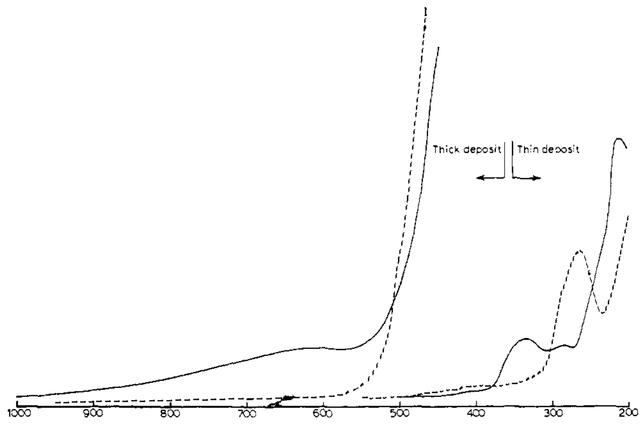

Figure 2. Electronic spectra of thermolysate of **3**: ——, at −196°; - - - - - -, at −100°.

distils off, the final spectrum being that of **4** (indicated below).

Deposition on a quartz plate was performed in two stages. A thin film permitted the determination of the high intensity absorption, and a thicker film (longer thermolysis) allowed the measurement of the low intensity absorption. The spectra obtained are shown in Figure 2, which we believe to be that of **1** with a trace of **3** or **4**. On warming from −196 to −100° the spectrum changed to that of **4**, and indeed reaction was observed from about −140°. The positions of S_1 and S_2 are in excellent agreement with those predicted by recent prior calculations.[8]

After warming it was shown in all cases that **4** and its isomer were the only products.

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[14] Holder of Canada Council Fellowship, 1970–1971; on leave from the C.N.R.S. Université de Paris, Sud.

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Ground and Excited States of Pentalene[1]

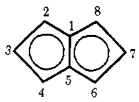
Sir:

The degree to which pentalene (**1**) should exhibit aromatic behavior has been a matter of interest and of controversy for half a century.[2–5]

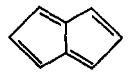
Although the parent hydrocarbon **1** has not yet been reported, the hexaphenyl derivative is known[6] and recent work in this institution has led to the generation of a highly reactive species believed to be methylpentalene.[7]

Given the instability of the latter compound, it would assist characterization studies if *quantitative* predictions of the electronic spectrum, structure, and aromaticity of pentalene itself could be made. For this reason, we wish to report calculations for the ground and lower excited states of **1**, using an MO method (NNDO) which has been shown to predict accurately, for a wide variety of hydrocarbons, the ground-state properties, uv spectrum, and lowest triplet energy using the same set of semiempirical parameters.[8]

As predicted originally by Longuet-Higgins[4] and subsequently confirmed by other MO calculations,[5,9] the singlet ground state of pentalene has the polyolefin structure **1b** of C_{2h} symmetry, rather than the "aromatic" D_{2h} structure **1a**; the NNDO calculations predict that the optimum **1b** structure is more stable than the optimum **1a** by 6.2 kcal mol^{-1}. Although the "polyene" geometry is preferred to the "aromatic," there are two indications that there is a *slight* degree of aromaticity associated with pentalene. First the average "double" bond distance of 1.358 Å is slightly longer than that of 1.345 ± 0.005 Å calculated for acyclic polyenes[8b] while the average "single" bond distance of 1.461 Å is slightly shorter than that of ~1.468 Å for polyenes.[8b,10] Secondly, the heat of formation (ΔH_f) calculated for the "strainless" molecule of +51 kcal mol^{-1} indicates that pentalene is 5 kcal mol^{-1} more stable than expected for a completely "nonaromatic" C_8H_6 hydrocarbon from the Dewar resonance energy method.[8c]



1a



1b

1c

If the total torsional strain energy in **1b** is assumed to be ~10 kcal mol^{-1}, the predicted ΔH_f is +61 kcal mol^{-1}. Thus pentalene should be very stable relative to decomposition into two acetylene and one diacetylene molecules, since this reaction should be endothermic[11] by ~231 kcal mol^{-1}.

Finally, the predicted ionization potential of 8.1 eV for **1b** is very close to that expected for a polyene with four double bonds.

In common with previous MO calculations[3,13] the NNDO method predicts a low-energy forbidden transition (659 nm, $f = 0$) due to the $\pi_4 \rightarrow \pi_5{}^*$ excitation in the singlet–singlet spectrum of **1b**. One-electron promotions from the other bonding MO's to the lowest vacant MO are predicted to lead to transitions in the ultraviolet region: $\pi_3 \rightarrow \pi_5{}^*$ at 335 nm ($f = 0.45$),

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[1] (a) Applications of Quantum Chemistry. II. For part I, see N. C. Baird, *Can. J. Chem.*, **49**, 338 (1971). (b) This research was supported by the National Research Council of Canada.

[2] J. W. Armit and R. V. Robinson, *J. Chem. Soc.*, **121**, 827 (1922).

[3] See Chapters I and IV in "Nonbenzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience, New York, N. Y., 1959.

[4] See H. C. Longuet-Higgins in "Theoretical Organic Chemistry; Kekulke Symposium," Butterworths, London, 1959.

[5] See M. J. S. Dewar in *Chem. Soc. Spec. Publ.*, **No. 21**, 177 (1967).

[6] E. Le Goff, *J. Amer. Chem. Soc.*, **84**, 3975 (1962).

[7] R. Bloch, R. A. Marty, and P. de Mayo, *ibid.*, **93**, 3071 (1971).

[8] (a) N. C. Baird, *Mol. Phys.*, **18**, 39 (1970); (b) N. C. Baird and R. M. West, *J. Amer. Chem. Soc.*, in press; (c) N. C. Baird, *J. Chem. Educ.*, in press.

[9] See, for example, P. C. den Boer-Veenendaal and D. H. W. den Boer, *Mol. Phys.*, **4**, 33 (1961).

[10] The actual bond distances (ångströms) calculated are 1.352, 1.455, 1.363, 1.473, and 1.451 for the C_1–C_2, C_2–C_3, C_3–C_4, C_4–C_5, and C_1–C_5 linkages, respectively.

[11] The ΔH for the reaction $C_8H_6 \rightarrow 2C_2H_2 + C_4H_2$ was calculated using the experimental[12] ΔH_f for C_2H_2 of +54.3 kcal mol^{-1} and estimating that for C_4H_2 as ~122 kcal mol^{-1} from analogy with the ΔH for $2HCN \rightarrow C_2N_2$ reaction.[12]

[12] J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, London, 1970.

[13] T. Nakajima, Y. Yaguchi, Y. Kaeriyama, and Y. Nemoto, *Bull. Chem. Soc. Jap.*, **37**, 272 (1964).