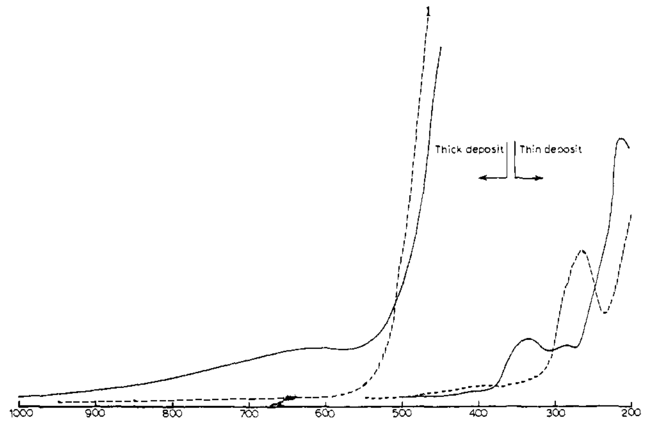

Figure 2. Electronic spectra of thermolysate of **3**: ——, at −196°; ------, at −100°.

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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Ground and Excited States of Pentalene[1]

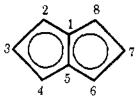
Sir:

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]

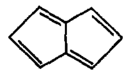
Although the parent hydrocarbon **1** has not yet been reported, the hexaphenyl derivative is known[6] and recent work in this institution has led to the generation of a highly reactive species believed to be methylpentalene.[7]

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_6 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).

$\pi_2 \rightarrow \pi_5^*$ at 273 nm ($f = 0.29$), and $\pi_1 \rightarrow \pi_5^*$ at 232 nm ($f = 0$). These λ_{max} values are in good agreement with the observed spectrum of hexaphenylpentalene[6] (λ_1 720 nm (log ϵ 1.95), λ_2 380 nm (log ϵ 3.99), and λ_3 310 nm (log ϵ 4.52)) if one assumes that the presence of the phenyl groups shifts each peak to lower energy by ~50 nm. The calculated positions and intensities for the first two transitions agree well with those observed[7] for methylpentalene, which has a broad, weak absorption at ~620 nm and strong bands at 335 and 210 nm.[14] The strong band observed at ~210 nm[7] cannot be due to the forbidden $\pi_1 \rightarrow \pi_5^*$ transition, and may well correspond to the allowed ($f \sim 1$) $\pi_4 \rightarrow \pi_6^*$ excitation predicted at 149 nm.

One of the interesting features predicted for pentalene is the relatively small energy difference of ~24 kcal mol^{-1} between the ground state and the lowest π–π^* triplet (both in their optimum geometries). Further, the equilibrium geometry of this triplet is predicted to be of D_{2h} symmetry, with calculated bond lengths of 1.412, 1.407, and 1.467 Å for the C_1–C_2, C_2–C_3, and C_4–C_5 linkages. Thus the lowest triplet is well represented by the symmetrical cyclooctatetraene structure **1c**.

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[14] There is some uncertainty as to whether the 285-nm band is due to methylpentalene or to its dimer.[7]

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Synthesis and Crystallographic Characterization of $[Me_4N^+]_2[Fe_6(CO)_{16}C^{2-}]$, a Hexanuclear Carbidocarbonyl Derivative of Iron

Sir:

Hexanuclear metal carbonyl species are known for elements of the cobalt triad (Co,[1] Rh,[2] Ir[3]) and for ruthenium,[4,5] but not for other transition metals. We now report the synthesis and characterization, by X-ray diffraction techniques, of a hexanuclear carbidocarbonyl derivative of iron, $[Me_4N^+]_2[Fe_6(CO)_{16}C^{2-}]$.

The reaction of $Fe(CO)_5$ with $[Mn(CO)_5^-]$ in diglyme has previously[6] been shown to yield the trinuclear "mixed-metal" anion, $[MnFe_2(CO)_{12}^-]$. However, a reinvestigation of this system reveals that $[Fe_6(CO)_{16}C^{2-}]$ is also formed in the reaction mixture and that the relative yields of the two anions are critically dependent on reaction conditions.

A solution of $NaMn(CO)_5$, obtained by the sodium amalgam reduction of $Mn_2(CO)_{10}$ (2 g) in dry diglyme (50 ml), was added to $Fe(CO)_5$ (4 ml) and the mixture was refluxed for 1 hr. A deep blue solution (characteristic of $[MnFe_2(CO)_{12}^-]$) was obtained after 5 min, but after 40 min the color of the solution had changed to red-brown. After cooling, the reaction mixture was added to water and the filtered aqueous solution was treated with an excess of Me_4NCl, yielding a red precipitate. This was dissolved in methanol; red-black crystals (2.5 g) of $[Me_4N^+]_2[Fe_6(CO)_{16}C^{2-}]$[7] were obtained after partial evaporation of the solution by a stream of N_2. The $[Fe_6(CO)_{16}C^{2-}]$ ion was also obtained by heating $[Et_4N^+][MnFe_2(CO)_{12}^-]$ in diglyme at 160°, thus indicating it to be a direct decomposition product of the mixed-metal anion.

The $[Fe_6(CO)_{16}C^{2-}]$ ion exhibits only four bands in the carbonyl stretching region: 1964 (s), 1957 (sh), 1930 (sh), 1775 (w, br) cm^{-1} (THF solution) or 1956 (sh), 1944 (s), 1925 (sh), 1750 (w, br) cm^{-1} (Nujol mull).

An X-ray crystallographic study of $[Me_4N^+][Fe_6(CO)_{16}C^{2-}]$ was undertaken in order to establish unequivocally the stereochemistry of the anion.

. The compound crystallizes in the centrosymmetric orthorhombic space group *Pnma* (D_{2h}^{16}; no. 62) with $a = 10.10$, $b = 18.79$, $c = 36.71$ Å, $V = 6961$ Å^3, $\rho_{calcd} = 1.891$ g cm^{-3} for mol wt 987.69 and $Z = 8$, $\rho_{obsd} = 1.82$ (2) g cm^{-3} (flotation in bromoform–hexane). No symmetry is necessarily imposed on the anion (however, *vide infra*).

Intensity data ($\sin \theta_{max} = 0.34$, Mo Kα radiation) for the levels $h(0–18)l$ and $(0–6)kl$ were collected with a Supper-Pace automated diffractometer, corrected for Lorentz, polarization, and absorption ($\mu = 24.38$ cm^{-1}) effects, and merged to a common scale. The structure was solved by Patterson, Fourier, and least-squares refinement techniques (anisotropic thermal parameters for iron atoms, isotropic for all other atoms). The final discrepancy index is $R_F = 11.9\%$ for the 1584 independent, nonzero reflections.[8]

The unit cell contains two sets of $[Me_4N^+]$ ions (each in a general position) and *two sets* of $[Fe_6(CO)_{16}C^{2-}]$ ions (each in special position 4c, and centered at 0.27, $^1/_4$, 0.13 and 0.23, $^1/_4$, 0.63). The two anions thus each have crystallographically imposed $C_s(m)$ symmetry and are geometrically equivalent. Dimensions referred to below are the mean of values within the two crystallographically independent dianions.

The essential geometry of the $[Fe_6(CO)_{16}C^{2-}]$ dianion is shown in Figure 1. There are 13 terminal carbonyl ligands; two per iron atom except for Fe(4), which is associated with three. (Fe(4) is also the only iron atom not to participate in a bridging carbonyl system.) There are three carbonyl bridges: Fe(5)–[C(1)–O(1)]–Fe(1) and the symmetry-related Fe(5)–[C(1′)–O(1′)]–Fe(1′), in which Fe(1)–C(1) = 1.79 (5) and Fe(5)–C(1) = 2.19 (5) Å; and the system Fe(2)–[C(5)–O(5)]–Fe(3), lying in the mirror plane of the dianion, in which Fe(2)–C(5) = 1.94 (6) and Fe(3)–C(5) = 2.16 (6) Å. Dimensions within these carbonyl

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[1] (a) P. Chini, *Chem. Commun.*, 29 (1967); (b) *ibid.*, 440 (1967); (c) V. Albano, P. Chini, and V. Scatturin, *ibid.*, 163 (1968); (d) *J. Organometal. Chem.*, **15**, 423 (1968); (e) P. Chini and V. Albano, *ibid.*, **15**, 433 (1968); (f) V. G. Albano, P. L. Bellon, P. Chini, and V. Scatturin, *ibid.*, **16**, 461 (1969); (g) P. Chini, *Inorg. Chem.*, **8**, 1206 (1969).

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[5] M. R. Churchill, J. Wormald, J. Knight, and M. J. Mays, *ibid.*, 458 (1970); M. R. Churchill and J. Wormald, *J. Amer. Chem. Soc.*, in press.

[6] U. Anders and W. A. G. Graham, *Chem. Commun.*, 291 (1966).

[7] *Anal.* Calcd for $C_{25}H_{24}Fe_6N_2O_{16}$: C, 31.7; H, 2.5; Fe, 35.5; N, 3.0. Found: C, 31.6; H, 2.7; Fe, 35.5; N, 3.2.

[8] The relatively high discrepancy index and low percentage of nonzero (*i.e.*, $>3\sigma$) reflections result from (i) the poor quality of obtainable crystals, (ii) decomposition of crystals within the X-ray beam.