been experimentally measured for any organic triplet molecules in solution but they can only be estimated theoretically.[15,16] We also emphasize here that under favorable conditions, the hydrogen abstraction rate (the pseudo-first-order rate, not the rate constant) of the triplet molecules can be comparable or even greater than the spin-lattice relaxation rate. For example, it has recently been estimated for *p*-benzoquinone in the laser-flash photolysis that the rate of hydrogen abstraction from solvent ethanol is[17,18] probably greater than $10^8$ sec$^{-1}$. Assuming the zero-field splitting of the n,$\pi^*$ triplet of 1,4-naphthoquinone is of the same order of magnitude of that of the n,$\pi^*$ triplet benzophenone,[19] the spin-lattice relaxation rate in the present system could be estimated theoretically[14,20] to be about $10^8$ sec$^{-1}$. Since the hydrogen abstraction rate is several times greater in 2-propanol than in ethanol,[21] it is probable that in the present system the hydrogen abstraction rate is greater than the spin-lattice relaxation rate of the triplet. Furthermore, as the Boltzmann population difference of the two levels is only about 0.75% of the total population, the hydrogen abstraction rate could even be one order of magnitude smaller than the spin-lattice relaxation rate and it would still be possible for an emissive spectrum to be observed.

A brief comparison of our present interpretation and the elegant "radical-pair" theory[6-9] is now given. The radical-pair theory is originally developed for the CIDNP phenomenon and beautifully accounts for most of the CIDNP experiments. While the radical-pair theory holds great potential in explaining certain CIDEP experiments, it cannot be taken as a universal mechanism for *all* CIDEP phenomenon. At the same time we do not hint that our proposed mechanism is a general one, because radicals are produced in different manners in different systems. Nevertheless, the main difference between the present mechanism and the radical-pair theory is that the latter is independent of the previous history in the formation of radicals. Because of this fundamental difference, it is possible to design further experiments to distinguish between these two mechanisms. For example, the radical-pair theory predicts that it is possible to observe anomalous population of the spin levels of radicals with uncorrelated spins.[9] However, there are many stable radicals[22] observed independent of the history of their formation and none has been reported to lead to anomalous population of the spin levels. Also according to the radical-pair theory, the radical pair should possess opposite polarization, whereas our proposed mechanism predicts the same polarization for the counter radical. A formal development of our proposed theory will be reported in a forthcoming paper.

**Acknowledgments.** This research is supported by the National Research Council of Canada. The authors are grateful to the referees for their helpful comments.

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*Received April 24, 1972*

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(15) R. Kubo and K. Tomita, *J. Phys. Soc. Jap.*, **9**, 888 (1954).

(16) I. Solomon, *Phys. Rev.*, **99**, 559 (1955).

(17) D. R. Kemp and G. Porter, *Proc. Roy. Soc., Ser. A*, **326**, 117 (1971).

(18) The absence of triplet–triplet optical absorption in the laser-flash photolysis of *p*-benzoquinone in ethanol has been interpreted as due to the very short lifetime (<10 nsec)[17] of the triplet quinone. From this we estimated that the hydrogen abstraction rate is probably greater than $10^8$ sec$^{-1}$.

(19) M. Sharnoff, *J. Chem. Phys.*, **51**, 451 (1969).

(20) Calculated from[16] $1/T_1 = (6\hbar^2\ \gamma^4/20b^6)\ [(\tau_c/1 + w^2\tau_c^2) + (4\tau_c/1 + 4w^2\tau_c^2)]$ where $\tau_c$ is the correlation time for 2-propanol at 20°, $\tau_c$ is calculated to be $6.64 \times 10^{-11}$ sec by taking 3.0Å as the radius of the tumbling molecule, and $b$ is the average electron–electron distance of 2.9 Å.

(21) G. Porter and M. R. Topp, *Proc. Roy. Soc., Ser. A*, **315**, 163 (1970).

(22) For example, see A. R. Forrester, J. M. Hay, and R. H. Thomson, "Organic Chemistry of Stable Free Radicals," Academic Press, New York, N. Y., 1968.

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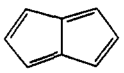
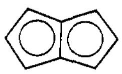
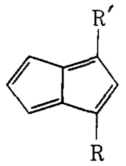
## A Stable Transition Metal $\pi$ Complex of Dimethylaminopentalene

*Sir:*

Pentalene (**1**), the lower homolog of naphthalene, has been the subject of considerable interest and controversy to both synthetic and theoretical chemists since 1922 when Armit and Robinson first suggested that this unique molecule might possess aromatic character.[1] Recent theoretical calculations are at odds with this early suggestion and predict that the singlet ground state of pentalene should be antiaromatic and possess the polyolefin structure **1a** rather than the delocalized structure **1b**.[2] Forbidden and allowed transitions in the uv region, bond distances, the heat of formation, and the ionization potential have all been calculated for the pentalene molecule.[2]


**1a**


**1b**



**2a**, R = R' = $(CH_3)_2N$
**b**, R = $CH_3$; R' = H

Unfortunately, experimental verification of these predictions has not been obtained since all attempts to prepare pentalene have met with failure.[3] Hexaphenyl-[4] and bis-1,3-dimethylaminopentalene (**2a**)[5] have been synthesized and shown to be relatively stable entities. In contrast, evidence supporting the existence of 1-methylpentalene (**2b**) could only be obtained by generating the molecule at −196° and determining its uv and ir spectra at the same temperature.[6] Dimerization of **2b** occurs rapidly above −100°.[6] Pentalene itself is also expected to be highly reactive and exhibit properties similar to **2b**.

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

(2) (a) See H. C. Longuet-Higgins, *Theor. Org. Chem., Pap. Kekule Symp.*, 17 (1959); (b) see M. J. S. Dewar, *Chem. Soc., Spec. Publ.*, No. 21, 177 (1967); (c) P. D. den Boer-Veéndaal and D. H. W. den Boer, *Mol. Phys.*, 4, 33 (1961); (d) N. C. Baird and R. M. West, *J. Amer. Chem. Soc.*, **93**, 3072 (1971).

(3) Original references may be found in the reviews of: (a) E. D. Bergmann in "Non-benzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience, New York, N. Y., 1959; (b) M. E. Vol'pin, *Usp. Khim.*, **29**, 298 (1960); (c) D. Lloyd, "Carbocyclic Non-Benzenoid Aromatic Compounds," Elsevier, New York, N. Y., 1966.

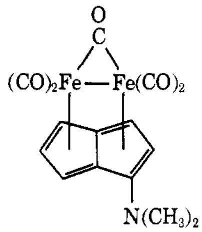
(4) E. L. Goff, *J. Amer. Chem. Soc.*, **84**, 3975 (1962).

(5) K. Hafner, K. F. Bangert, and V. Orfanos, *Angew. Chem., Int. Ed. Engl.*, **6**, 451 (1967).

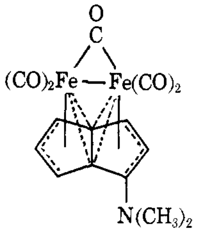
(6) R. Bloch, R. A. Marty, and P. de Mayo, *J. Amer. Chem. Soc.*, **93** 3071 (1971).

Like cyclobutadiene,[7] trimethylenemethane,[8] and heptafulvene,[9] pentalene should be greatly stabilized as a result of coordination to a transition metal. The recent synthesis of bis(pentalenylnickel),[10] diallyldihydropentalenylenedinickel,[11] tetraallyldihydropentalenylenedichromium,[11] and hexallyldihydropentalenylenedizirconium[11] provides support for this thesis and suggests that it may be possible to prepare additional organometallic derivatives which will serve as a source of free pentalene itself.

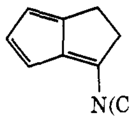
In this report we describe the preparation and physical properties of (*octahapto*-1-dimethylaminopentalene)-$\mu$-carbonyltetracarbonyldiiron(Fe–Fe) (**3**), a stable transition metal $\pi$ complex of dimethylaminopentalene.



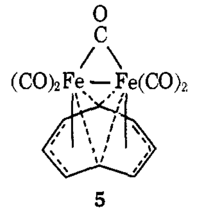
**3a**



**3b**



**4**



**5**

A solution containing 3-dimethylamino-1,2-dihydropentalene (**4**)[12] (290 mg, 2.0 mmol), iron pentacarbonyl (5 ml, 37 mmol), and 25 ml of deoxygenated methylcyclohexane was heated at 105° under nitrogen for 12 hr. The reaction mixture was then cooled, filtered, and concentrated under reduced pressure (20 mm). Preparative tlc of the residue on neutral silica gel using 9:1 benzene–acetone as the eluent afforded 85 mg (11%) of **3** as a green-black solid, mp 113–115° ($N_2$). *Anal.* Calcd for $C_{10}H_{11}NFe_2(CO)_5$: C, 45.39; H, 2.79; N, 3.53. Found: C, 45.78; H, 3.01; N, 3.47.

In the EI mass spectrum (70 eV) of **3** strong peaks corresponding to the molecular ion and fragments resulting from the successive loss of five carbonyls and two iron atoms appear at $m/e$ 397 (11), 369 (15), 341 (16), 313 (21), 285 (64), 257 (100), 201 (29), and 145 (49). Confirmation of the molecular weight was obtained from the CI($CH_4$) mass spectrum[13] which shows an abundant M + 1 ion at $m/e$ 398. The infrared spectrum ($CCl_4$) of **3** exhibits three bands (2025, 1987, 1957 $cm^{-1}$, all $\pm 5$ $cm^{-1}$) in the terminal CO region and one band at 1760 $\pm$ 5 $cm^{-1}$ in the bridging CO region. The 100-MHz nmr spectrum (acetone-$d_6$) of **3** shows signals at $\tau$ 4.56 (1, t, $H_5$), 5.24 and 6.17 (2, pair of doublets, $J_{5,6} = J_{4,5} = 2.5$ Hz, $H_{4,6}$), 5.09 (1, d, $J_{2,3} = 3$ Hz, $H_3$), 6.31 (1, d, $H_2$), and 7.29 (6, s, $(CH_3)_2N$). Assignments were confirmed by double-resonance experiments.

The above spectral data are consistent with either formulation **3a** or **3b** for the dimethylaminopentalene $\pi$ complex and differentiation of these two possibilities must await X-ray analysis. It is interesting to note that cyclooctatetraene also forms a diiron pentacarbonyl complex[14] which has been shown to have structure **5**.[15] Unlike **3**, the cyclooctatetraene complex **5** exhibits fluxional behavior at room temperature.

Preliminary experiments with phenyldihydropentalene[12] and also with dihydropentalene itself[16] indicate that the procedure described above will prove to be a general method for preparing iron carbonyl complexes of pentalenes.[17] Work is presently underway to complete the characterization of several additional complexes and to explore the chemistry of the coordinated pentalene nucleus.

**Acknowledgment.** We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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(17) Treatment of phenyldihydropentalene with $Fe(CO)_5$ and dihydropentalene with either $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ affords diiron pentacarbonyl complexes of phenylpentalene and pentalene as indicated by mass spectral analysis of the reaction mixtures.

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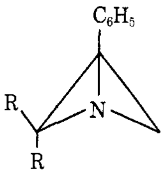
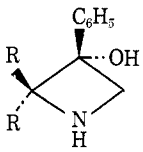
## An Inverse $\beta$-Deuterium Isotope Effect in the Solvolysis of a 1-Azabicyclo[1.1.0]butane

*Sir:*

We wish to report the observation that $k_H/k_D$ = 0.948 for the relative rates of acid-catalyzed hydrolysis of 3-phenyl-1-azabicyclo[1.1.0]butane (**1a**) and its 2,2-dideuterio analog (**1b**). This isotope effect is consistent with a completely inductive or field transmission of the effect of $\beta$-deuterium substitution and places severe constraints on the kinds of bonding which can be present in the transition state.



**1a**, R = H
**b**, R = D



**2a**, R = H
**b**, R = D

The syntheses of **1a,b** have been described elsewhere.[1] The solvolysis rates were measured by the previously

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