Table I. Thermodynamic and Kinetic Parameters for an Alkyl Group Migration in Iridium(III) Complexes $\{IrCl_2[C(O)R][P(C_6H_5)_3]_2\}_{solid} \longrightarrow \{IrCl_2(CO)(R)[P(C_6H_5)_3]_2\}_{solid}$

R	T,[a] °K	ΔH_T,[b] kJ mol⁻¹	Standard deviation of ΔH_T (kJ mol⁻¹)	$\int_{298}^{T} \Delta C_p dT$ (kJ mol⁻¹)	ΔH_0, kJ mol⁻¹	$t_{1/2}$ (in solution) (min)	$\Delta H^{\ddagger}$ (in solution) (kJ mol⁻¹)
Ia, CF_3	445	−83.88	3.8	0.08	−84 ± 4	44.59[d] (at 343 °K)	+86.5
Ib, p-$NO_2C_6H_4CH_2$–	444	−16.40	1.30	0.01	−16 ± 1	29.67[d,e] (at 303 °K)	+84.5[d]
Ic, p-$CH_3C_6H_4CH_2$–	428	−14.39	1.51		−14 ± 2[c]	13.83[d,e] (at 303 °K)	+68.2[d]
Id, p-$CH_3OC_6H_4CH_2$–	419	−13.34	3.81		−13 ± 4[c]	12.57[d,e] (at 303 °K)	+62.8[d]

[a] Temperature of peak maximum. [b] Each value is the average of 12 determinations. [c] $\Delta H_0 = \Delta H_T$ by analogy with compounds Ia and Ib. [d] Ia in toluene, Ib, c, and d, in benzene. [e] M. Kubota, D. Blake, and S. Smith, *Inorg. Chem.*, **10**, 1430 (1971).

Table II. Heat Capacity Data, $C_p = (a + bT + cT^2 + dT^3)$ (4.184 J °K⁻¹ mol⁻¹)

Compound[a]	a	b	c	d	$\int_{298}^{T} C_p dT$ (kJ mol⁻¹)	T[b]
$IrCl_2[C(O)CF_3]L_2$	179.49	1.8279×10^{-1}	-2.0533×10^{-3}	4.83×10^{-6}	131.67	445 °K
$IrCl_2(CO)CF_3L_2$	128.26	−1.2987	7.5246×10^{-3}	9.02×10^{-6}	131.75	
$IrCl_2[C(O)CH_2C_6H_4NO_2]L_2$	−39.686	1.3955	-2.8362×10^{-3}	3.01×10^{-6}	145.81	444 °K
$IrCl_2(CO)(CH_2C_6H_4NO_2)L_2$	−71.013	2.4474	-779.67×10^{-3}	9.29×10^{-6}	145.82	

[a] $L = P(C_6H_4)_3$. [b] T = temperature at which the migration reaction occurs.

data are shown in Table I. In order to determine the enthalpy change at standard conditions, ΔH_0, the following relation was used

$$\Delta H_0 = \Delta H_T - \int_{298}^{T} \Delta C_p dT$$

Molar heat capacities, C_p, were determined for the pairs of compounds Ia and IIa and Ib and IIb using differential scanning calorimetry.[4c] The data for C_p as a function of temperature were fitted to a third degree polynomial equation in T from 298° to the reaction temperature for each compound. The integrals were then evaluated using Simpson's rule.[5] These data are shown in Table II. The magnitude of the integral term for ΔC_p was much smaller than the standard deviation in ΔH_T so that ΔH_0 may be assumed to be equal to ΔH_T. These data are shown in Table I, along with kinetic data for the reaction in homogeneous solution.

The magnitude of the enthalpy change is smaller than metal–carbon monoxide bond energies (*ca.* 120–170 kJ mol⁻¹)[6] or metal–carbon bond energies (*ca.* 150–300 kJ mol⁻¹).[7] The enthalpy change is opposite in sign from that found for the decarbonylation of benzoyl platinum complexes (eq 4) for which ΔH = +18.6 to

$$[P(C_6H_5)_3]_2PtCl[C(O)C_6H_4X] \longrightarrow [P(C_6H_5)_3]_2PtCl(C_6H_4X) + CO \quad (4)$$

+33.9 kJ mol⁻¹ depending on the substituents on the phenyl group.[8] In this reaction the carbon monoxide does not remain coordinated to the metal.

From the data it can be noted that there is an inverse correlation between the migration rate and the enthalpy change. The enthalpy change in solution is anticipated to be close in value to that in the solid state since heats of solution of the compounds I and II are likely to be small and of similar magnitude in nonpolar solvents. The large difference in the magnitude of ΔH_0 for the trifluoromethyl, −83 kJ mol⁻¹, and benzyl groups, *ca.* −15 kJ mol⁻¹, is noteworthy. The enthalpy change for the migration reaction includes four bond energy terms (Ir—C≡O, Ir—C(O)R, Ir—R, and C(O)—R). Unfortunately there is not at present sufficient information available about the individual contributions to make a meaningful discussion of the difference in the overall values of ΔH possible. A kinetic and calorimetric study is now in progress for the series of five-coordinated complexes analogous to I where R = CF_nH_{3-n} (n = 3, 2, 1, or 0). Preliminary results show that the enthalpy change for reaction 3 decreases in the series $CF_3 > CF_2H > CFH_2 > CH_3 \approx p$-$XC_6H_4CH_2$. Other work is in progress to extend the data to other migrating groups and to seek correlations of the enthalpy changes with kinetic and spectral parameters of the complexes.

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(9) (a) Robert A. Welch Foundation Predoctoral Fellow. (b) Supported in part as a Robert A. Welch Foundation Undergraduate Fellow and by funds from the University Organized Research Fund.

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(6) H. A. Skinner, *Advan. Organometal. Chem.*, **2**, 49 (1964).

(7) G. Wilkinson, *Pure Appl. Chem.*, **30**, 627 (1972).

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MINDO/3 Study of the Bisdehydrobenzenes

Sir:

While the three bisdehydrobenzenes **1**, **2**, and **3** were characterized some years ago by Berry, *et al.*,[1–3] while the ortho isomer **1** (benzyne) has been proposed as an

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(1) R. S. Berry, G. N. Spokes, and M. Stiles, *J. Amer. Chem. Soc.*, **84**, 3570 (1962).

(2) R. S. Berry, J. Clardy, and M. E. Shafer, *Tetrahedron Lett.*, 1003 (1965).

(3) R. S. Berry, T. Clardy, and M. E. Shafer, *Tetrahedron Lett.*, 1101 (1965).

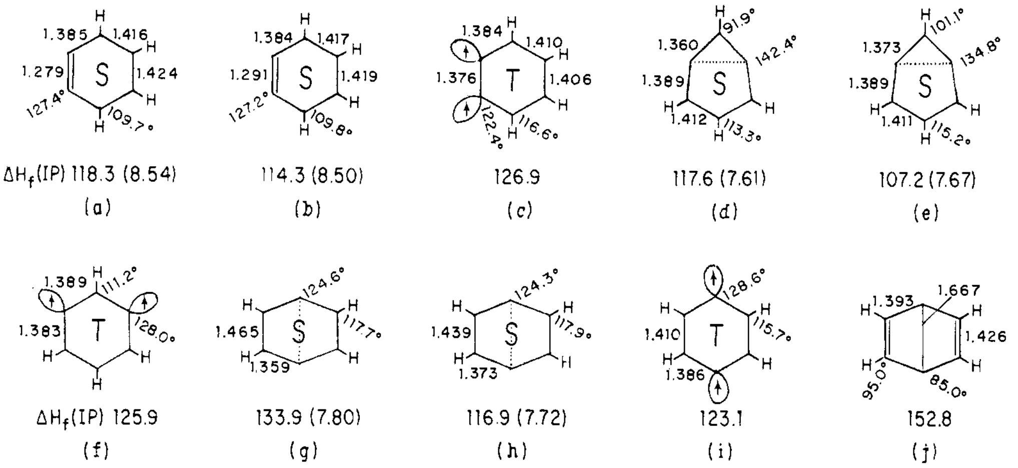
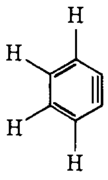


Figure 1. Calculated bond lengths (Å), bond angles, heats of formation (ΔH_f, kcal/mol at 25°), and ionization potentials for singlet *o*-(a), *m*-(d), and *p*-(g) benzyne without CI; for singlet *o*-(b), *m*-(e), and *p*-(h) benzyne with CI; for triplet *o*-(c), *m*-(f), and *p*-(i) benzyne; and for **5** (j). The transition state for conversion of **5** to **3** has ΔH_f = 157.5 kcal/mol.

intermediate in numerous reactions,[4] and while the other two isomers (**2**, **3**) have also recently been postulated as reaction intermediates,[5,6] doubt remains concerning their structures, and few meaningful theoretical studies have been reported. Thus the *ab initio* SCF calculations of Millie, *et al.*,[7] and of Wilhite and Whitten[8] were based on the unrealistic assumption that the geometries of **1**–**3** are similar to that of benzene and the same is true of the EH calculations by Hoffmann, *et al.*,[9] and the CNDO/2 by Atkin and Claxton.[10] The correspondingly uncertain conclusions from these calculations are that **1** has a singlet ground state[8,10] while **2** and **3** have triplet ground states,[8] that the order of stability is **1** > **3** > **2**,[9] and that the heat of formation (ΔH_f) of **1** is 72.6 kcal/mol.[7] The latter value agrees poorly with the only available experimental extimate (118 ± 5 kcal/mol[11]). Haselbach[12] has reported a MINDO/2 study of **1**, with complete optimization of the geometry, that led to a more satisfactory estimate of ΔH_f (107 kcal/mol).

It is impossible to make meaningful predictions concerning the multiplicities of **2** and **3** without considering their geometries because the singlet forms might well collapse to the bicyclohexatrienes **4** and **5**. This problem cannot be meaningfully treated in terms of MINDO/2 because this procedure is known to underestimate strain energies.[13] MINDO/2 calculations[14] indeed predicted **4** and **5** to have ΔH_f that were obviously too low.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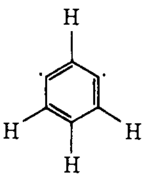
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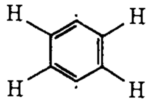
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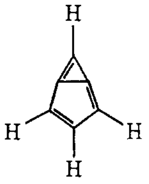
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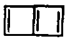
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The development of an improved version of MINDO (MINDO/3[15]), in which the strain energy problem has been solved, led us to reinvestigate this problem.

Calculations were carried out for the singlet and triplet forms of **1**, **2**, and **3**, the geometry being optimized with respect to all geometrical variables and the calculations for the triplets being based on the "half-electron" approximation.[16] Since the standard MINDO treatment is liable to give too positive heats of formation for "biradical" species such as **2** or **3**, the singlet calculations were also carried out with inclusion of CI with the first doubly excited configuration.[17] Since MINDO/3 has not been parametrized with inclusion of such CI,[17] the energies found in this way will be too negative. However, tests have shown that the ΔH_f for normal molecules are depressed only 2–3 kcal/mol by such inclusion of CI.

The calculated properties of all six species are listed in Figure 1. Those for the singlets are shown with and without CI. All the molecules were predicted to be planar. The calculated heats of formation of singlet **1** (118.4 kcal/mol without CI, 114.2 kcal/mol with) are seen to agree well with experiment (118 ± 5 kcal/mol[11]) and the differences between the two values for this "normal" molecule are small. Note that the distortions from benzenoid geometry (small 1,2 bond length, large 123 and 612 bond angles) are those expected and note also that the remaining CC bond lengths are similar, implying retention of benzenoid aromaticity.

The geometries of singlet **2** and **3** imply strong bonding between the "radical" centers, the 1,3 distance in **2**

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(4) See, *e.g.*, R. W. Hoffmann, Ed., "Dehydrobenzene and Cycloalkynes," Academic Press, New York, N. Y., 1967.

(5) See, *e.g.*, H. E. Bertorello, R. A. Rossi, and R. H. de Rossi, *J. Org. Chem.*, **35**, 3332 (1970).

(6) See, *e.g.*, R. R. Jones and R. G. Bergmann, *J. Amer. Chem. Soc.*, **94**, 660 (1972).

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(9) R. Hoffmann, A. Imamura, and W. H. Hehre, *J. Amer. Chem. Soc.*, **90**, 1499 (1968).

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(11) H. T. Gruetzmacher and J. Lohman, *Justus Liebigs Ann. Chem.*, **705**, 81 (1967).

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(13) See M. J. S. Dewar, *Fortschr. Chem. Forsc.*, **23**, 1 (1971).

(14) Unpublished work by M. S. Kohn. The results for **1** agree with those of Haselbach.[12]

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(17) See R. C. Bingham and M. J. S. Dewar, *J. Amer. Chem. Soc.*, **94**, 9107 (1972).

and the 1,4 distance in **4** being less than in benzene. The effect is greater for the normal MINDO/3 calculations than for those with CI, as one would expect since the energies calculated for biradical species without CI are too large.[17] The geometry thus tends to approximate more closely to that of an equivalent nonradical structure (*e.g.*, **4** instead of **2**).

We also studied the energies of singlet **2** and **3** as a function of the distance between the "radical" centers. In the case of **2** only one minimum was found (Figure 1d, e, but with **3** there were two minima, one corresponding to **3** (Figure 1g, h, and the other to **5**. Thus **3** or **5** is predicted to exist in two isomeric forms with different C_1C_4 distances. The second isomer is also predicted to be a distorted benzene (Figure 1j) with a very long transannular bond (1.667 Å) and little variation of bond lengths round the ring. The calculated ΔH_f (152.8 kcal/mol) is much higher than that for **3** from which it is separated only by a low barrier (4.6 kcal/mol). In the transition state the C_1C_4 distance is 1.85 Å.

All calculations[8,10] agree in predicting the singlet form of **1** to be the more stable. Those reported here differ, however, from previous ones[8] in predicting **2** to have a singlet ground state. Since this is true both with and without CI, the prediction seems very strong. The opposite conclusion reached in the earlier calculation could then well be due to use of an unrealistic geometry for the singlet.

In the case of **3** the calculations are more ambiguous, those without CI predicting the ground state to be a triplet and those with CI a singlet. It seems likely that the ground state is in fact a singlet but with a small singlet–triplet separation. The *ab initio* calculations[8] could well have led to the opposite conclusion through use of an incorrect geometry.

The most striking prediction from our calculations is that singlet **2** should be at least comparable in stability with singlet **1** (*cf.* Hess and Schaad[18]). This suggests that more consideration should be given to reaction mechanisms involving *m*-benzynes (*e.g.*, **2**) as intermediates.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research through Contract F44620-71-C-0119 and by the Robert A. Welch Foundation through Grant F-126.

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(19) Robert A. Welch Postdoctoral Fellow.

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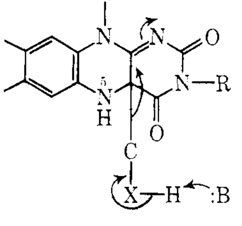
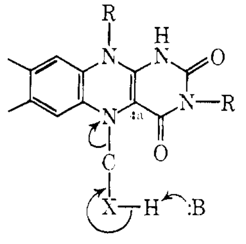
A Kinetic Study of the Fate of a Covalent Intermediate of the Type Proposed to be Involved in Flavin Catalysis

Sir:

A non-free-radical[1] (dark) flavin oxo–reduction reaction not involving hydrogen transfer[2,3] from substrate to flavin would require the formation of a covalent intermediate. Based on chemical intuition[4] and photoreduction[5] studies the site of covalent adduct formation has been suggested to be the 4a- and 5-positions, I and II, respectively. A 5-carbinolamine adduct has been suggested as an intermediate in the reaction of nitroethane anion with oxidized deuterated amino acid oxidase,[6] but this same adduct has been shown not to be an intermediate in the reduction of formaldehyde and ethyl pyruvate by reduced flavin.[1,3] No direct chemical evidence exists which establishes a 4a-adduct as an intermediate in a flavin catalyzed reaction though addition of SO_3^{2-} to the 4a-position has been established for one isoalloxazine.[7]


I (4a-adduct)


II (5-adduct)

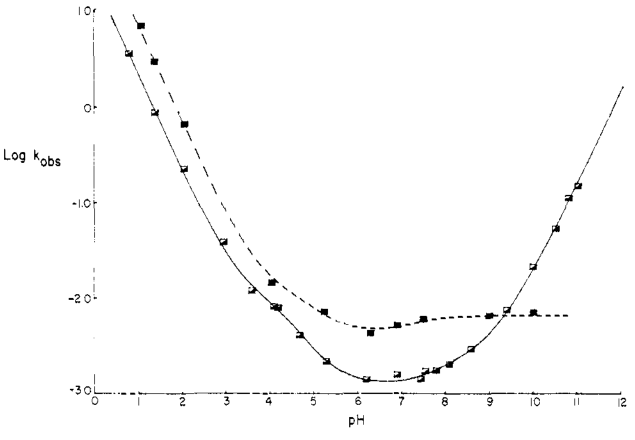


Figure 1. Log k_{obsd} *vs.* pH rate profile for solvolysis of 4a-InH (——) and 4a-InMe (----): Solvent H_2O (aerobic), 30°, $\mu = 0.2$. Rate constants in min^{-1}. The E-2 elimination for 4a-InH may be seen in the slope of +1.

In aqueous solution (30°, $\mu = 0.2$ with KCl), the solvolysis of 4a-InH and 4a-InMe yields dihydroflavin (FH_2) under anaerobic conditions and oxidized flavin (F_{ox}) under aerobic conditions.[8] The pH–log k_{obsd}

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(1) S. Shinkai, M. Brüstlein, R. F. Williams, and T. C. Bruice, to be submitted to *Biochemistry*.

(2) M. Brüstlein and T. C. Bruice, *J. Amer. Chem. Soc.*, 94, 6548 (1972).

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(6) D. J. T. Porter, J. G. Voet, and H. J. Bright, *J. Biol. Chem.*, 248, 4400 (1973).

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(8) 4a-InH (λ_{max} 353 nm; ϵ 6200 M^{-1} cm^{-1} in acetonitrile) and 4a-InMe (λ_{max} 355 nm; ϵ 5400 M^{-1} cm^{-1} in acetonitrile) were obtained (Ph.D. Dissertation, W. R. Knappe, University of Konstanz, 1971, Germany) by photolysis under argon of absolute acetonitrile solutions of 3-Me lumiflavin and 40-fold excesses of indole-3-acetic acid and 1-methylindole-3-acetic acid, respectively. Rate runs were initiated by introducing 0.1 ml of the acetonitrile stock solution into 3 ml of oxygenated or degassed water or 50% ethanol–water (v/v) and observing the increase in absorbance of F_{ox} (441 nm) and decrease in absorbance of 4a-adducts (376 nm at low pH and 370 nm at high pH). 3-Hydroxymethylindole was identified as product at both acidic and baisc pH under both anaerobic and aerobic conditions *via* chromatography on silica employing three different solvent systems by comparison of R_f values to that of the authentic compound and *via* reaction with *sym*-trinitrobenzene.