dioxocane. Interconversion of these forms, a process analogous to pseudorotation in cyclooctane, does not lead to mutual exchange of the two protons on C-2, but does lead to exchange of C-4 with C-8, and C-5 with C-7. As expected, the barrier (5.7 kcal/mol) for this process is lower than that (7.3 kcal/mol) for ring inversion. The conformational picture here is analogous to that of cyclooctanone, which shows corresponding barriers of 6.3 and 7.5 kcal/mol. Interestingly, the dihedral angles in the conformations given above for the fragment $CH_2OCH_2OCH_2$ correspond to those found in dimethoxymethane[13] and thus represent a low-energy geometry.

The two remaining compounds, 1,3,6-trioxocane (III)[14] and 1,3,5,7-tetroxocane (IV),[15] show rather similar behavior in that each exists as a mixture of two conformations in solution. The proton spectrum of III at 25° consists of two sharp singlets at τ 5.25 and 6.45 with relative intensities of 1:4. Upon cooling, the signals broaden and by −100° the low-field line has changed into a widely spaced AB quartet which contains within it a sharp singlet. The AB quartet represents one conformer (A), where ring inversion is slow, and the singlet a second conformer (B), where ring inversion is rapid. At the same temperature (−100°), the high-field pattern consists of an intense singlet superposed on a multiplet. At still lower temperatures (−150°), the low-field singlet of conformer B becomes a narrowly spaced AB quartet, while changes in the high-field line are obscured by extensive overlap with signals from conformer A. The ratio ($\simeq$1:1) of these two conformations shows essentially no temperature dependence from −100 to −150°.

At 25°, the proton spectrum of 1,3,5,7-tetroxocane (IV) consists of a broad line at τ 4.96 which sharpens markedly on heating to 40°. As the temperature is lowered to −40° the spectrum of IV changes to a widely spaced AB quartet (conformation A) and a singlet (conformation B) near the center of the quartet. Although the singlet broadens somewhat near −160° it does not become a resolved AB quartet as does the rather similar singlet of III under the same conditions. Also, in contrast to III, the relative intensities of the forms A and B are strongly temperature dependent, indicating an entropy difference of 6 ± 2 eu, with the A form favored at low temperatures. At −86°, $K(A \rightleftharpoons B)$ is 0.17.

With III and IV, boat-chairs should become less favorable, because of repulsions between transannular oxygen atoms. The widely spaced AB quartets in the A forms of III and IV are in striking contrast to the narrowly spaced AB quartets of II and the B forms of III and IV. Tentatively, more or less twisted boat-chairs are assigned to the B conformations. The A forms of III and IV likely are twist chair-chair and symmetrical crown forms, respectively.[16,17] Further experiments, including the determination of ^{13}C spectra, are in progress.

Acknowledgments. We thank Professor J. Dale and Drs. T. Ekeland and J. Krane for informing us of their results[18] on some of the compounds discussed in the present paper. We also thank the National Science Foundation and the United States Public Health Service for support of this research.

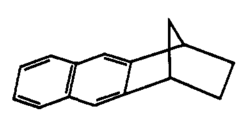
(13) J. K. Wilmshurst, *Can. J. Chem.*, 26, 285 (1958).
(14) P. A. Laurent and P. Tarte, *Bull. Soc. Chim. Fr.*, 718 (1960).
(15) Y. Miyake, S. Adachi, N. Yamauchi, T. Hayashi, and M. Akimoto, U. S. Patent 3,426,041 (1969); *Chem. Abstr.*, 70, 87867 (1969).
(16) These assignments are consistent with the large entropy difference between the A and B forms of IV, since the crown form of IV has a C_4 axis, whereas the twisted boat-chair has no symmetry axes and furthermore exists in *d* and *l* forms. The entropy difference resulting from these symmetry affects is $3R \ln 2$ or 4.2 eu, with the A form of lower entropy, as found experimentally.
(17) X-Ray diffraction studies on three different saturated eight-membered rings with heteroatoms in the 1, 3, 5, 7 positions show that these compounds possess crown conformations: L. Pauling and D. C. Carpenter, *J. Amer. Chem. Soc.*, **58**, 1274 (1936); D. Grandjean and A. Leclaine, *C. R. Acad. Sci.*, **265**, 795 (1967); H. Schenck, *Acta Crystallogr., Sect. B*, 27, 185 (1971). A tetrabromocyclooctane, on the other hand, has been found to have a twist chair–chair conformation: G. Ferguson, D. D. MacNicol, W. Oberhanshi, R. A. Raphael, and J. A. Zabkiewicz, *Chem. Commun.*, 103 (1968).
(18) J. Dale, T. Ekeland, and J. Krane, *J. Amer. Chem. Soc.*, **94**, 1389 (1972).

F. A. L. Anet,* P. J. Degen
Contribution No. 2883
Department of Chemistry, University of California
Los Angeles, California 90024
Received November 22, 1971

A Spectroscopic Study of Some Dibromonaphthonorbornenes. A Possible Case of "Inverse" External Heavy Atom Induced Spin Orbital Coupling[1]

Sir:

We report a study at 77°K in EPA of the fluorescence and phosphorescence of the dibromonaphthonorbornenes **2–5**. A comparison of these new data with those formerly reported[2] for **6**, **7**, and **8** reveals interesting



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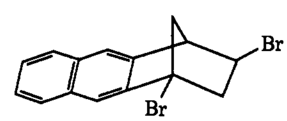

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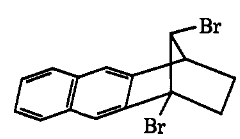

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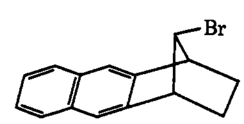

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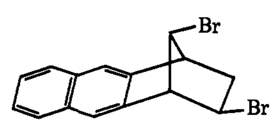

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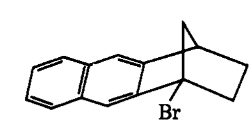

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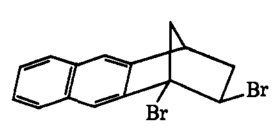

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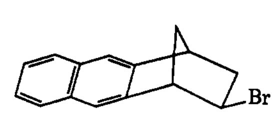

8

and unexpected effects on spin orbital coupling when two external heavy atoms perturb the naphthalene chromophore.

(1) (a) Molecular Photochemistry. LI. Paper L: A. Yekta and N. J. Turro, *Mol. Photochem.*, 3, 307 (1972). (b) The authors wish to thank the Air Force Office of Scientific Research for its generous support of this work (Grant No. AFOSR-70-1848).
(2) G. Kavarnos, T. Cole, Jr., P. Scribe, J. C. Dalton, and N. J. Turro, *J. Amer. Chem. Soc.*, 93, 1032 (1971).

Table I. Spectroscopic and Kinetic Data of Naphthonorbornenes in EPA[a] at 77°K

Molecule	ϕ_p/ϕ_F[b]	ϕ_p[b]	ϕ_F[c]	τ_p, sec	k_p, sec^{-1} [d]	k_D, sec^{-1} [e]	k_{IS}, sec^{-1} [f]
1	0.14	0.057	0.41	3.7	0.026 (1)	0.24 (1)	1.5×10^6 (1)
2	311	1.0	0.003	0.13	7.7 (300)	≪0.7 (≪0.3)	3.1×10^8 (210)
3	88	0.76	0.009	0.082	9.4 (360)	2.8 (12)	1.1×10^8 (70)
4	69	0.39	0.006	0.12	3.3 (130)	5.1 (21)	1.8×10^8 (120)
5	121	0.58	0.005	0.20	2.9 (110)	2.1 (9)	2.1×10^8 (140)
6	140	0.56	0.004	0.11	5.1 (196)	4.0 (17)	2.5×10^8 (170)
7	32	0.32	0.010	0.34	0.95 (37)	2.0 (8)	9.9×10^7 (66)
8	14	0.25	0.018	0.31	0.82 (32)	2.4 (10)	5.5×10^7 (37)

[a] Ether–isopentane–ethanol glass (5:5:2). The numbers in the parentheses are rates relative to **1**. [b] 280-nm excitation radiation on a Hitachi Perkin-Elmer spectrophosphorimeter; corrected for differences in detector response. Phosphorescence areas were normalized with respect to the phosphorescence area of naphthalene. The optical densities at the excitation radiation (at room temperature) were also normalized with respect to naphthalene. The ratios of normalized phosphorescence areas to normalized optical densities were then multiplied by the literature value of $\phi_p = 0.03$ [V. L. Ermolaev, *Sov. Phys. Usp.*, 6, 333 (1963)] for naphthalene to give absolute ϕ_p values. The differences between the ether–ethanol glass used by Ermolaev and the EPA used in this work should be negligible. Had the literature value of $\phi_p = 0.05$ [E. H. Gilmore, G. E. Gibson, and D. S. McClure, *J. Chem. Phys.*, **20**, 829 (1952); **23**, 399 (1955)] in EPA been chosen as the naphthalene standard, our ϕ_p values would be well above unity, which seems improbable. The values of ϕ_p, nevertheless, are internally consistent and probably quite precise (±10%). [c] Calculated from ϕ_p/ϕ_F and ϕ_p. [d] $k_p = (1/\tau_p)(\phi_p/1 - \phi_F)$. The derivation of k_p and k_D requires that internal conversion from the first excited singlet state is negligible. This assumption is generally true for aromatic molecules in rigid media at low temperature: V. L. Ermolaev and E. B. Sveshnikova, *Opt. Spectrosc.*, **16**, 320 (1964). [e] $k_D = k_p\{[1 - (\phi_p + \phi_F)]/\phi_p\}$. See footnote *d*. [f] $k_{IS} = (\phi_p/\phi_F)(k_F/k_p)(k_D + k_p)$. k_F is assumed to be 1×10^6 sec^{-1}, the value for naphthalene at room temperature. The radiative $\tau_F{}^0$ is very slightly temperature dependent (2–48°): I. B. Berlman, *Mol. Cryst.*, **4**, 157 (1968). Since the extinction coefficients for the series do not differ by very much, the relative lifetime of the singlet is not expected to vary significantly (less than a factor of 2).

Table I summarizes our data which consist of accurate measurement of the ratio ϕ_p/ϕ_F and the phosphorescence lifetimes. From these data and information in the literature concerning ϕ_p and τ_f for naphthalene, we were able to evaluate the values of the rate constants k_{IS} ($S_1 \rightarrow T_1$), k_p ($T_1 \rightarrow S_0 + h\nu$), and k_D ($T_1 \rightarrow S_0 + \Delta$).

One of the main purposes of this study was to see how the addition of a second bromine atom to the norbornene framework would influence the spin orbital coupling already set up by the first bromine atom.

From Table I it can be seen that in general for the dibromides, k_p and k_{IS} have values by factors of 2–3 greater than any of the monobromides **6**, **7**, or **8** (**6** is an exception in some cases). Addition of a second bromine to **7** or **8** to produce **4** increases k_D, but to a lesser extent than k_p. However, addition of a second bromine to **6** to produce **2** and **3** serves to *decrease* k_D, thereby implying an inverse heavy atom effect on the radiationless transition $T_1 \rightarrow S_0$.

Inverse heavy atom effects have been reported in the quenching of the fluorescence of substituted anthracenes.[3] These results, however, may be due to special perturbations of the T_2 state of anthracenes, since this state[4] is very close in energy to S_1. Thus, solvent and solute perturbations may significantly modify the energetic position of T_2 relative to S_1 and/or the ability of T_2 and S_1 to undergo spin orbital mixing. Such effects could well lead to special behavior of fluorescence from S_1 in the presence of heavy atoms.

A more intriguing phenomenon has been observed in a study of the effect of ethyl bromide on the fluorescence and phosphorescence of naphthalene in cyclohexane glasses at 77°K.[5] In this case, it was found that the enhancement of phosphorescence by added ethyl bromide reached a maximum at about 10% ethyl bromide, and then fell sharply. However, it was not established whether or not the influence of ethyl bromide had "saturated" the radiative rate k_p but continued to enhance the radiationless rate k_D.

In our previous communication[2] we reported that the spectroscopic data at 77°K of a series of monobromonaphthonorbornenes indicated that the position of the bromine atom on the rigid norbornene framework was crucial in determining the degree of mixing between the singlet and triplet electronic states of the naphthalene chromophore, as measured by the effects of bromine position on the emission lifetimes and yields. The rate constants of intersystem crossing ($S_1 \rightarrow T_1$ (k_{IS})), phosphorescence ($T_1 \rightarrow S_0$ (k_p)), and radiationless deactivation ($T_1 \rightarrow S_0$ (k_D)) each displayed a different sensitivity to bromine substitution, suggesting a different combination of mechanisms, including spin orbital coupling. The kinetic data of *anti*-7-bromonaphthonorbornene showed the largest heavy atom effect on these rates. This is especially surprising, since the syn and endo molecules possess a bromine atom which is spatially closer to the naphthalene chromophore than the bromine atom of the anti-7 compound.

According to a relativistic conception of the theory of spin orbital coupling,[6] the change in the spin angular momentum of an electron that accompanies a change in its spin is made possible by a corresponding change in the orbital angular momentum of a nucleus in its vicinity, thus conserving total momentum during the lifetime of the spin inversion. This interaction between the spin and angular momenta is then expected to be proportional to the electrostatic field gradient of the nucleus of the perturbing atom(s). Based upon this rather naive description, spin orbital coupling should be enhanced by any one of the following conditions: (1) a large atomic number of the nucleus; (2) a close proximity of the nucleus to the optical electron; (3) an increase in the number of interacting heavy-atom nuclei.

Many experimental investigations[7] have shown that

(3) A. Kearvell and F. Wilkinson, *Mol. Cryst.*, **4**, 69 (1968).

(4) R. G. Bennett and P. J. McCartin, *J. Chem. Phys.*, **44**, 1969 (1966).

(5) T. H. Bolotnikova and O. N. Sichkar, *Opt. Spectrosc.*, **28**, 43 (1970).

(6) S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State," Prentice-Hall, Englewood Cliffs, N. J., 1969, Chapter 5.

(7) (a) See ref 6, Chapters 6–8; (b) M. Kasha, *J. Chem. Phys.*, **20**, 71 (1952); (c) M. Kasha, *Radiat. Res. Suppl.*, 2, 243 (1960).

spin orbital coupling is influenced by conditions 1 and 3, with respect to both the internal and external heavy atom effects.[8] Since few data existed to verify condition[9] 2, we undertook the investigation of the monobromonaphthonorbornenes. Quite surprisingly, we did not find a direct relation between the distance of the heavy atom from the chromophoric naphthalene and the degree of singlet–triplet state mixing. As mentioned above, we considered this as good evidence for other mechanisms[7a,b] in addition to spin orbital coupling, such as spin vibronic coupling and photochemistry. The results also made it necessary to invoke a special role to the back lobe of the carbon–bromine bond in electronic state mixing. The data on the dibromonaphthonorbornenes reported in this paper further serve to emphasize the complex mechanisms involved in the heavy atom effect, especially those governing radiationless deactivation of the triplet state.

(8) See ref 6, Chapters 7 and 8.
(9) (a) K. B. Eisenthal, *J. Chem. Phys.*, **45**, 1850 (1966); (b) N. K. Chaudhuri and M. A. El-Sayed, *ibid.*, **45**, 1358 (1966).

Nicholas J. Turro,* George Kavarnos, Victor Fung
A. L. Lyons, Jr., Theron Cole, Jr.
Department of Chemistry, Columbia University
New York, New York 10027
Received November 2, 1971

Oscillations in Chemical Systems. I. Detailed Mechanism in a System Showing Temporal Oscillations

Sir:

Belousov[1] first observed temporal oscillations in a sulfuric acid solution containing bromate and cerium ions and malonic acid. Figure 1 presents the simul-

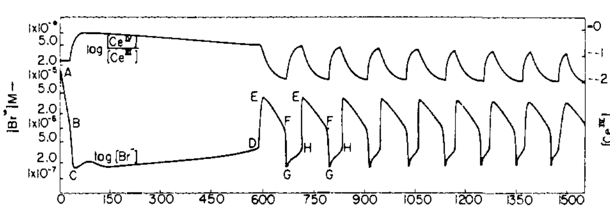

Figure 1. Potentiometric traces at room temperature of log [Br^-] and of log [Ce(IV)]/[Ce(III)] for a stirred solution in which the initial concentrations were [$CH_2(COOH)_2$] = 0.032 *M*, [$KBrO_3$] = 0.063 *M*, [KBr] = 1.5×10^{-5} *M*, [$Ce(NH_4)_2(NO_3)_5$] = 0.001 *M*, and [H_2SO_4] = 0.8 *M*.

taneous behavior in such a system of electrodes sensitive to bromide ion activity and to cerium(IV)/cerium(III) ratio. Studies by several investigators[2–4] have obtained additional information but have not elucidated the mechanism. We now present a detailed mechanism supported by quantitative information about the elementary processes involved. No attempt is made here to explain the spatial oscillations observed[5,6] in the same system.

In an acid solution of bromate and malonic acid containing sufficient bromide ion, the sequence (R3) +

$$BrO_3^- + Br^- + 2H^+ \longrightarrow HBrO_2 + HOBr \quad (R3)$$

$$HBrO_2 + Br^- + H^+ \longrightarrow 2HOBr \quad (R2)$$

$$HOBr + Br^- + H^+ \longrightarrow Br_2 + H_2O \quad (R1)$$

$$Br_2 + CH_2(COOH)_2 \longrightarrow BrCH(COOH)_2 + Br^- + H^+ \quad (R8)$$

(R2) + 3(R1) + 3(R8) results in net process A. Let

$$BrO_3^- + 2Br^- + 3CH_2(COOH)_2 + 3H^+ \longrightarrow 3BrCH(COOH)_2 + 3H_2O \quad (A)$$

rate constant subscripts correspond to R numbers. We have confirmed the observation of Bray and Liebhafsky[7] that at 25° $k_3 = 2.1\ M^{-3}\ sec^{-1}$. If the free energy of formation of BrO_2^- calculated by Lee and Lister[8] is used to estimate the free energy of $HBrO_2$ and combined with the kinetics reported by Betts and MacKenzie[9] for the decomposition of HOBr, then $k_2 = 4 \times 10^9\ M^{-2}\ sec^{-1}$. Eigen and Kustin[10] observed $k_1 = 1.6 \times 10^{10}\ M^{-2}\ sec^{-1}$. The rate of (R8) is controlled by the acid-catalyzed enolization of malonic acid, which is usually sufficient to remove bromine as rapidly as it is formed in our system.

These numbers clearly support the kinetic inference that step R3 is rate determining for process A. When this process is taking place, the concentration of bromous acid attains a steady state given by eq 1. As is ex-

$$[HBrO_2]_A = \frac{k_3}{k_2}[BrO_3^-][H^+] = 5 \times 10^{-10}[BrO_3^-][H^+] \quad (1)$$

pected from the proposed mechanism, the rate of process A is independent of the presence or absence of cerium(III).

When bromide ion is virtually absent, bromate ion reacts with cerium(III) and malonic acid such that the sequence 2(R5) + 4(R6) + (R4) + (R8a) results in net

$$BrO_3^- + HBrO_2 + H^+ \longrightarrow 2BrO_2\cdot + H_2O \quad (R5)$$

$$BrO_2\cdot + Ce^{3+} + H^+ \longrightarrow HBrO_2 + Ce^{4+} \quad (R6)$$

$$2HBrO_2 \longrightarrow BrO_3^- + HOBr + H^+ \quad (R4)$$

$$HOBr + CH_2(COOH)_2 \longrightarrow BrCH(COOH)_2 + H_2O \quad (R8a)$$

process B. Thompson and we[11] have pointed out that

$$BrO_3^- + 4Ce^{3+} + CH_2(COOH)_2 + 5H^+ \longrightarrow BrCH(COOH)_2 + 4Ce^{4+} + 3H_2O \quad (B)$$

the kinetic data of Thompson[12] indicate (R5) is rate determining for this sequence, and the data of Betts and MacKenzie[13] indicate the same step is rate determining for the isotopic exchange of bromate with elementary bromine giving $k_5 = 1.2 \times 10^4\ M^{-2}\ sec^{-1}$. Then the Thompson[12] data indicate that $k_4 = 6 \times 10^7\ M^{-1}\ sec^{-1}$. Of course (R8a) is stoichiometrically equivalent to (R1) + (R8), and its rate is determined by the same enolization reaction.

(1) B. P. Belousov, *Sb. Ref. Radiats. Med., 1958, Medgiz, Moscow*, 1 (1959).
(2) A. A. Vavilin and A. M. Zhabotinskii, *Kinet. Katal.*, 10, **83**, 657 (1969).
(3) H. Degn, *Nature (London)*, 213, 589 (1967).
(4) G. J. Kasperek and T. C. Bruice, *Inorg. Chem.*, 10, 382 (1971).
(5) H. G. Busse, *J. Phys. Chem.*, 73, 750 (1969).
(6) A. N. Zaikin and A. M. Zhabotinskii, *Nature (London)*, **225**, 535 (1970).
(7) W. C. Bray and H. A. Liebhafsky, *J. Amer. Chem. Soc.*, **57**, 51 (1935).
(8) C. L. Lee and M. W. Lister, *Can. J. Chem.*, **49**, 2822 (1971).
(9) R. H. Betts and A. N. MacKenzie, *ibid.*, **29**, 666 (1951).
(10) M. Eigen and K. Kustin, *J. Amer. Chem. Soc.*, **84**, 1355 (1962).
(11) R. M. Noyes, R. J. Field, and R. C. Thompson, *ibid.*, **93**, 7315 (1971).
(12) R. C. Thompson, *ibid.*, **93**, 7314 (1971).
(13) R. H. Betts and A. N. MacKenzie, *Can. J. Chem.*, **29**, 655 (1951).