bridged structure 3.[11] Further confirmation is provided by the observed coupling constants. According to the Casabella–Bray–Barnes treatment,[9] the coupling constant for a bridged aluminum compound $Al_2X_6$ should be given approximately by

$$e^2Qq = 37.52(b - a)(1 + \eta/3)^{-1} \qquad (2)$$

where $a$ and $b$ are the electron densities in a bridging Al orbital and a terminal orbital, respectively. Thus, replacement of a bridging alkyl group by an electronegative group, e.g., halogen, should reduce $a$ and so increase the coupling constant, while analogous replacement of a terminal alkyl group should reduce $b$ and so decrease the coupling constant. In agreement with this we see a rapid increase in $e^2Qq$ along the series $AlBr_3$ (14 MHz), $RAlCl_2$ (26 MHz), $R_2AlX$ (37 MHz); each replacement of one terminal halogen per aluminum in the dimer by alkyl increases $e^2Qq$ by ca. 12 MHz. Conversely, replacement of the final halogen leads to a decrease from 37 MHz for $R_2AlX$ to 24 MHz for $R_3Al$, i.e., a change of 6 MHz for each Al for each bridging group. Since the three-center bond linking the bridging group X can be regarded as a covalent bond from X to an $Al_2$ unit, changes in X should alter the orbital density in each aluminum by about half the amount for a corresponding change in a normal Al–X bond; replacement of bridging halogen by alkyl should therefore lower the coupling constant by about one-half the amount that corresponding replacement of terminal halogen raises it.

These preliminary studies therefore seem to emphasize the potential utility of nqr as a tool for studying the structure of compounds of this type and also the bonding involved in them. It is true that most of the structures deduced here agree with current intuition; however, there has been as yet little direct evidence for them. The measurement of nqr spectra is also much less time consuming than structure determination by X-ray or electron diffraction while deductions from nmr are usually complicated by the possibility of rapid interchange of terminal and bridging groups.

(11) This has been indicated for Me$_2$AlCl in the gas phase by electron-diffraction studies: L. O. Brockway and N. R. Davidson, *J. Amer. Chem. Soc.*, **63**, 3287 (1941).

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## External Heavy-Atom-Induced Spin–Orbital Coupling. Spectroscopic Study of Naphthonorbornanes[1]

*Sir:*

According to present theory,[2] spin–orbital coupling provides the crucial mechanism which allows the otherwise "forbidden" interconversion of the singlet and triplet states of organic molecules. By studying the factors which affect spin–orbital coupling, we can hope to better understand the nature of forbidden radiationless and radiative electronic transitions. The magnitude of spin–orbital coupling in most organic molecules is strongly dependent on the atomic number of nuclei in the vicinity of the optical (orbitally decoupled) electrons. The effect of directly affixed internal[3] heavy (third row of the periodic table and beyond) atoms and external[4] (solvent) heavy atoms on the singlet–triplet interconversions of organic molecules has been the focus of much theoretical[5] and experimental work.[4a,d,e,6] Although spin–orbital coupling induced by external heavy-atom perturbation has been shown in some cases[2,5] to be quite significant, hardly any data exist on how the heavy-atom effect varies as a function of geometry and distance between a chromophore and a nonconjugated perturber.[7] It has been assumed that a collision complex[2] or its equivalent is required for effective spin–orbital perturbation of a chromophore (e.g., naphthalene or its derivatives) and an external heavy atom (e.g., an alkyl halide).[5] Whether charge transfer[2c,8] or electron exchange[2c,9] would be a predominant mechanism of spin–orbital interaction in such a complex, although a matter of considerable interest, is still a matter of controversy. The external heavy-atom effect has been used[5] (a) as a probe for the mechanism of molecular electronic state mixing, (b) to enhance sensitivity in phosphorimetry, and (c) to enhance intersystem crossing in photochemical studies.

We have prepared and investigated the emission spectroscopy of a series of monobromonaphthonorbornanes (II–VII) in which the position of the halogen atom is systematically varied among all of the unique positions of the norbornane framework. The rigidity of the bicyclic [2.2.1]heptene system allows us to precisely estimate the position[10] in space of the bromine atom relative to the naphthalene chromophore.

The results of our investigation are quite striking and are summarized in Table I. Of considerable interest is the observation that there is no obvious general relationship between the distance of the bromine atom from the naphthalene nucleus and the magnitude of spin–orbital coupling as measured by the values of $k_{IS}$ ($S_1 \rightarrow T_1$), $k_P$ ($T_1 \rightarrow S_0 + h\nu$), and $k_D$ ($T_1 \rightarrow S_0 + \Delta$).[11]

(1) (a) Molecular Photochemistry. XXXIX. Paper XXXVIII: J. C. Dalton and N. J. Turro, *Annu. Rev. Phys. Chem.*, **21**, 499 (1970); paper XXXVII: N. C. Yang, E. D. Feit, M. H. Hui, N. J. Turro, and J. C. Dalton, *J. Amer. Chem. Soc.*, **92**, 6974 (1970). (b) The authors gratefully acknowledge the Air Force Office of Scientific Research for its generous support of this research.

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*Radiat. Res., Suppl.*, **2**, 243 (1960); (c) G. W. Robinson, *J. Chem. Phys.*, **46**, 572 (1967).

(3) (a) M. Kasha, *Discuss. Faraday Soc.*, No. **9**, 14 (1950); (b) P. Yuster and S. I. Weissman, *J. Chem. Phys.*, **17**, 1182 (1949); (c) D. S. McClure, *ibid.*, **17**, 905 (1949).

(4) (a) S. P. McGlynn, R. Simseri, and N. Christodouleas, *ibid.*, **37**, 1818 (1962); (b) J. Nag-Chaudhuri, L. Stoessell, and S. P. McGlynn, *ibid.*, **38**, 2037 (1963); (c) S. P. McGlynn, M. J. Reynolds, G. W. Daigre, and N. D. Christodouleas, *J. Phys. Chem.*, **66**, 2499 (1962); (d) S. P. McGlynn, J. Daigre, and F. J. Smith, *J. Chem. Phys.*, **39**, 675 (1963); (e) S. Siegel and H. S. Judeikis, *ibid.*, **42**, 3060 (1965).

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(7) (a) K. B. Eisenthal, *ibid.*, **45**, 1850 (1966); (b) N. K. Chaudhuri and M. A. El-Sayed, *ibid.*, **45**, 1358 (1966).

(8) S. P. McGlynn, *Chem. Rev.*, **58**, 1113 (1958).

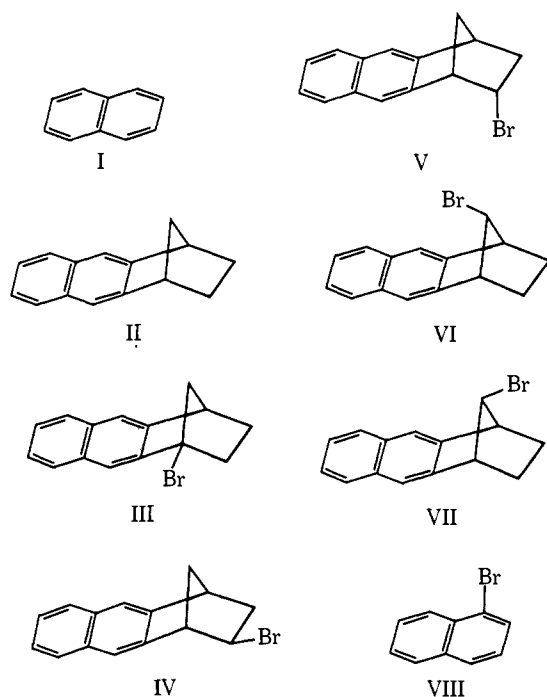(9) G. J. Hoijtink, *Mol. Phys.*, **3**, 67 (1960).

(10) The naphthonorbornanes were synthesized by simple modifications of the syntheses of the corresponding benzonorbornanes reported and unambiguously characterized by J. W. Wilt and P. J. Chenier, *J. Org. Chem.*, **35**, 1562 (1970).

**Table I.** Spectroscopic and Kinetic Data of Naphthonorbornanes in EPA$^a$ at 77°K

| Molecule | $\phi_P/\phi_F{}^b$ | $\phi_P{}^b$ | $\phi_F{}^c$ | $\tau_P$, sec$^d$ | $k_P$, sec$^{-1\,e}$ | $k_D$, sec$^{-1\,f}$ | $k_{IS}$, sec$^{-1\,g}$ |
|---|---|---|---|---|---|---|---|
| I | 0.09 | 0.03 | 0.33 | 2.4 | 0.019 | 0.41 | $2.0 \times 10^6$ |
| II | 0.14 | 0.057 | 0.41 | 3.7 | 0.026 (1) | 0.24 (1) | $1.5 \times 10^6$ (1) |
| III | 32 | 0.32 | 0.010 | 0.34 | 0.95 (37) | 2.0 (8) | $9.9 \times 10^7$ (66) |
| IV | 14 | 0.25 | 0.018 | 0.31 | 0.82 (32) | 2.4 (10) | $5.5 \times 10^7$ (37) |
| V | 46 | 0.47 | 0.010 | 0.25 | 1.9 (73) | 2.1 (9) | $9.7 \times 10^7$ (65) |
| VI | 6.1 | 0.45 | 0.07 | 0.77 | 0.63 (24) | 0.67 (3) | $1.3 \times 10^7$ (9) |
| VII | 140 | 0.56 | 0.004 | 0.11 | 5.1 (196) | 4.0 (17) | $2.5 \times 10^8$ (170) |
| VIII | 275$^h$ | 0.16 | 0.001 | 0.014 | 11 (423) | 58 (240) | $5.2 \times 10^9$ (3500)$^i$ |

$^a$ Ether:isopentane:ethanol glass (5:5:2). The numbers in parentheses are rates relative to II. $^b$ 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. Emolaev, *Sov. Phys. Usp.*, **6**, 333 (1963)] for naphthalene to give absolute $\phi_P$'s. 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. Gilison, and D. S. McClure, *J. Chem. Phys.*, **20**, 829 (1952); **23**, 399 (1955)] in EPA been chosen as the naphthalene standard, our $\phi_P$'s would be well above unity, which seems improbable. The values of $\phi_P$, nevertheless, are internally consistent and probably quite precise ($\pm 10\%$). $^c$ Calculated from $\phi_P/\phi_F$ and $\phi_P$. $^d$ We wish to acknowledge the assistance of Arthur Lyons and Ahmed Yekta in obtaining the triplet lifetimes. $^e$ $k_P = (1/\tau_P)(\phi_P/1 - \phi_F)$. $^f$ $k_D = k_P\{[1 - (\phi_P + \phi_F)]/\phi_F\}$. $^g$ $k_{IS} = (\phi_P/\phi_F)(k_F/k_P)(k_D + k_P)$. $k_F$ is assumed to be $1 \times 10^6$ sec$^{-1}$, the value for naphthalene at room temperature. [See ref 3c. The radiative $\tau_F{}^0$ is very slightly temperature dependent (2–48°): I. B. Berlman, *Mol. Crystals*, **4**, 157 (1968).] Since the extinction coefficients for the series do not differ by very much, the radiative lifetime of the singlet is not expected to vary significantly (less than a factor of 2). $^h$ See references of footnote $b$. $^i$ $k_F = 3 \times 10^6$ sec$^{-1}$.$^{3c}$

The following salient observations, however, are to be noted in Table I: (1) $k_{IS}$ and $k_P$ (which increase substantially for III–IV relative to II) vary with bro-



mine substitution on the norbornane framework, the values among the various bromine positions differing by up to a factor of 19; (2) the variation in $k_D$, while enhanced in all cases, does not parallel those of $k_{IS}$ and $k_P$. These observations reinforce the view[5] that "heavy-atom effects" on the processes $S_1 \rightarrow T_1$, $T_1 \rightarrow S_0 + h\nu$, and $T_1 \rightarrow S_0 + \Delta$ may be characterized by different mechanisms.

The first-order theoretical description for spin-orbital coupling[2b] states that the radiative process,

phosphorescence, is enhanced by an increase in the atomic number ($Z$) of a perturbing center, the magnitude of the interaction of the optical electrons with the available nuclei, and, to a lesser extent, by a decrease in the energy separation between the triplet and singlet ground state. Thus, an increased spin-orbital perturbation should result in a larger $k_P$. This is best demonstrated in the case of V, for which $k_P$ is greater than $k_P$ for VI by a factor of 3. This result may obtain in part from the fact that for V the bromine p$\pi$ orbital overlaps the naphthalene p$\pi$ orbitals to a greater extent than in VI.

Although differences in energy spacing with bromine atom substitution do not seem to alter the state densities significantly enough to influence the radiative process (the $E_T$'s (0–0 band) do not differ markedly), they may play an important role in intersystem crossing.

A most interesting effect is seen in the case of VII, which displays the highest $k_{IS}$ and $k_P$ values of the norbornane series. An intriguing, but speculative, explanation attributes a special role in spin-orbital perturbation to the back lobe of the bromine p$\pi$ orbital.

The lack of a correlation between the $k_D$'s and the trends in $k_P$ and $k_{IS}$ (observation 2) implies that some complex dependence on factors besides spin-orbital coupling may be occurring in the radiationless process. The presence of accessible vibrational modes and possibly photochemistry[12] may assist in the radiationless deactivation path. We are presently turning our attention to both the photochemistry at room temperature of compounds III–VII and the spectral data of their deuterated analogs to test these suggestions.

Perhaps the most anomalous data in Table I are the rate constants for VIII. It should be noted from Table I, however, that the data for 1-bromonaphthalene come from several possibly inconsistent sources. Thus, a comparison with the data of the naphthonorbornane series is somewhat unsatisfactory.

In summary, the behavior of molecules II–VII indicates that bromine atoms affect $k_{IS}$, $k_P$, and $k_D$ in

(11) For evidence that $k_P$ is enhanced by an external heavy atom to a larger extent than $k_D$, see K. B. Eisenthal and M. A. El-Sayed, *J. Chem. Phys.*, **41**, 749 (1964); ref 4e; G. G. Giachino and D. R. Kearns, *ibid.*, **52**, 2964 (1970); T. H. Bolotnikova and O. N. Sichkar, *Opt. Spectrosc.*, **28**, 21 (1970). For a somewhat different point of view, see ref 4d.

(12) Review: R. K. Sharm and N. Kharasch, *Angew. Chem., Int. Ed. Engl.*, **7**, 36 (1968).

several ways and that the position of the bromine atom is an important factor in determining the degree of interaction between singlet and triplet electronic states.

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## The Color of Liquid Sulfur

Sir:

At the melting point, liquid sulfur is yellow; at the boiling point it is dark red. The color change, which is demonstrated in every freshman class, is due to an apparently monotonous shift of the absorption edge toward the red and to an increase of the visible absorption (Figure 1). While the accompanying vis-
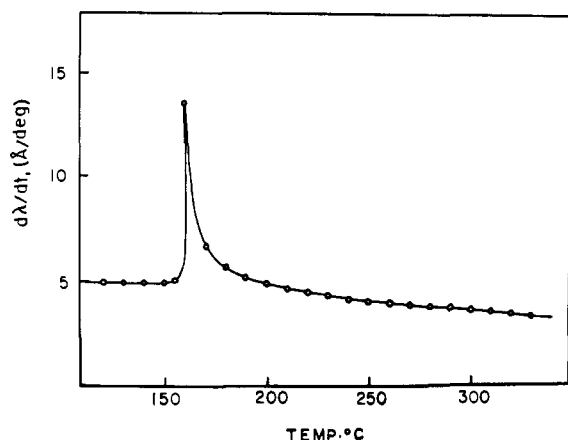


Figure 1. Shift of red absorption edge of liquid sulfur.

cosity change is well known and well understood,[1,2] the color change has drawn little scientific attention.

Only three spectral studies have been reported,[3-5] and the latest view[5] is that the shift of the absorption edge is caused by thermal population of ground-state vibrational modes of $S_8$.

We have studied the absorption spectrum of liquid sulfur in the temperature range between the melting point and 700°C. The temperature-dependent shift of the red absorption edge is about 23.6 cm$^{-1}$ per degree.[6] This shift is two times larger than the shift of the red absorption edge of $S_8$ in solution in the temperature range between 76°K and 25°C.[6] The shift in the liquid is too large to be due to thermal population

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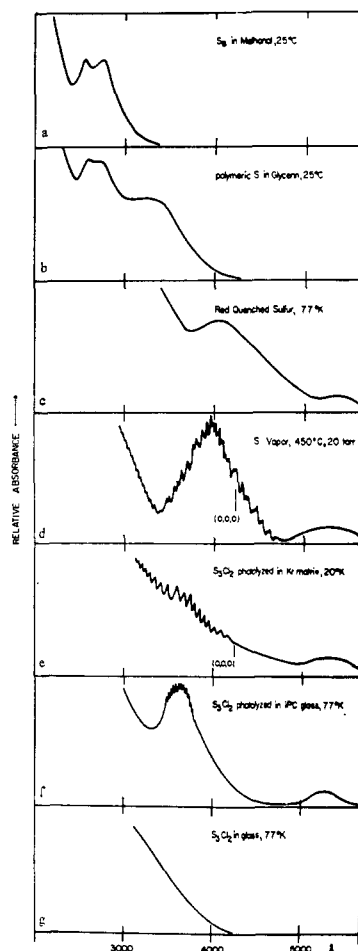(6) T. V. Oommen, Ph.D. Thesis, University of Washington, Seattle, 1970.



Figure 2. (a) Absorption of $S_8$ in methanol at 25°C. (b) Absorption of polymeric sulfur in glycerin at room temperatue. (c) Absorption of boiling sulfur quenched in liquid nitrogen. (d) Absorption of sulfur vapor at 450°C and 20 Torr. (e) Absorption of $S_8Cl_2$ photolyzed in a krypton matrix at 20°K. (f) Absorption of $S_8Cl_2$ photolyzed in 1:2 isopentane–cyclohexane glass at 77°K. (g) $S_8Cl_2$ before photolysis.

alone. Furthermore, the temperature-dependent shift is only reversible if the liquid is very slowly cooled. Rapid quenching of the liquid to room temperature does not yield the absorption of $S_8$, as shown in Figure 2a, but it yields the spectrum in Figure 2b. The shoulder at 3600 Å is due to quenched, metastable polymeric sulfur.[6] The formation, concentration, and composition of polymers in liquid sulfur are well established.[1,2] The spectrum of polymeric sulfur explains the apparently large shift in the spectrum of the liquid between the melting point and 300°C and the sudden increase of the shift at 160°C.

However, above 300°C, where the concentration of polymers decreases, the color of the liquid continues to darken If boiling sulfur is quenched in liquid nitrogen, we obtain a red glass with the spectrum shown in Figure 2c. At about −80°C the red films convert into yellow polymeric sulfur. The quenching experiments prove that the spectrum of hot liquid sulfur is not due to thermal broadening of $S_8$ absorption alone, but due to superposition of the spectrum of $S_8$ with that of polymeric sulfur and that of the red species which absorb at 4000 and 5100 Å.

In order to identify the red species, we compared the spectrum of the liquid with that of the vapor at 17 Torr