Table III. Substituent Chemical Shifts for Some Anthracene Adducts

Solvent	Substituent chemical shift, ppm[a]						
	OCOCH$_3$	Cl	Br	CO$_2$CH$_3$	CN	NHCOCH$_3$	NO$_2$
			Maleic Anhydride Adducts				
1,4-Dioxane	+0.03	−0.52	−0.87	−0.91	−0.41	−0.50	−0.65
Dimethylformamide	−0.18	−0.57	−0.94	−1.01	−0.43	−0.58	−0.80
Acetone	−0.11	−0.57	−1.00	−1.03	−0.48	−0.66	−0.86
Methanol	*b*	−0.54	−0.91	−0.98	−0.41	*b*	*b*
			Ethylene Adducts				
Carbon tetrachloride	*c*	*c*	−2.00	−2.05[d]	−0.50	*c*	*c*

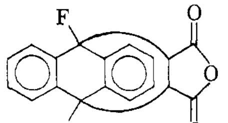
[a] Measured as noted in ref 8. [b] Not sufficiently soluble for measurement. [c] Not examined. [d] The carboxylic acid rather than the ester was examined.

The ^{19}F chemical shifts of these fluorides exhibit a large dependence on the character of the *tertiary* carbon atom. The upfield shifts observed for the more strained compounds are not in accord with the prediction that an increase in the s character of the exocyclic bonding orbital should produce a downfield shift.[9] These upfield shifts are, however, compatible with the idea that the bond order is larger[3] in these strained molecules because there is an important interaction between the nonbonding electrons of the fluorine atom and the endocyclic carbon–carbon bonds with enhanced p character.

The substituent effects that were observed for the 4-substituted bicyclo[2.2.2]octyl fluorides (I)[10] are presented in Table II.

These data are incompatible with both empirical and theoretical predictions for the polar effect of electron-withdrawing substituents on the chemical shift.[4] However, the positive SCS may be rationalized on the basis of the idea that there is an important repulsive interaction between the more electropositive bridgehead carbon atoms of the disubstituted bicyclic molecules leading to an elongation of the structure and an increase in the p character of the endocyclic carbon–carbon bonds. If future work verifies this suggestion it is evident that ^{19}F resonance may prove valuable for the detection of even modest changes in structure.

The SCS values for the maleic anhydride (II) and ethylene (III) adducts of anthracene were also measured. The results are summarized in Table III.



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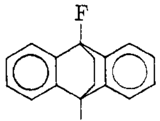

III

Inasmuch as the dibenzobicyclo[2.2.2]octa-2,5-diene skeleton is not easily deformed, we believe that the SCS values presented in Table III reflect the correct sign and magnitude of the polar effects of substituents in this environment. The small shifts are compatible with Buckingham's theory[5] which predicts, for example, that SCS for the 4-chloro and 4-bromo derivatives should be about −0.4 ppm. Although it is evident that other factors must influence the SCS values in these molecules, it seems safe to conclude that polar effects (whether inductive or electric field in origin) have a modest influence on the chemical shifts of the bicyclic compounds.

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The Role of Second Triplet States in Solution Photochemistry. I. Reactions of Rigid Systems Sensitized by Anthracene and Substituted Anthracenes

Sir:

We wish to report here a case of triplet–triplet energy transfer involving the T$_2$ state of the donor molecule.

The donors used in our studies are anthracene and substituted anthracenes. The energy diagram of anthracene[1] is shown in Figure 1. The acceptors used are several rigid systems, **1–4**, which have well-identified unimolecular triplet-state reactions.[2–4] Because of geometric restrictions, it is obvious that "nonvertical" excitations[5,6] involving distortion of the double bonds

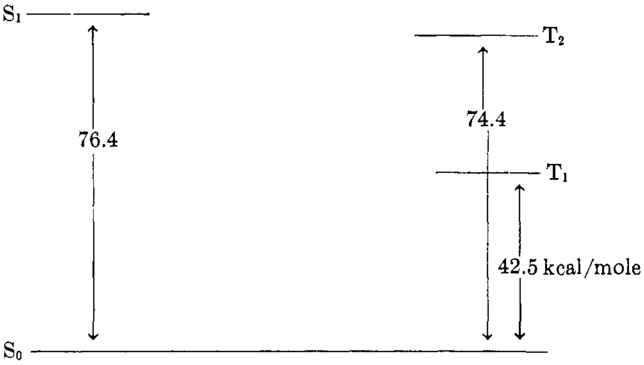
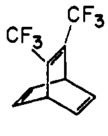


Figure 1. Energy diagram of anthracene.



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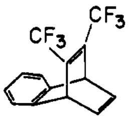

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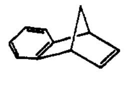

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(8) The chemical shifts were determined by the side-band technique with either tetrachlorotetrafluorocyclobutane or hexafluorobenzene as internal references using Varian HR 56 or HA 56-60 equipment.

(9) The smaller chemical shifts for the bridgehead hydrogen atoms in comparable hydrocarbons are in the opposite order: K. Tori, Y. Hata, R. Muneyuki, Y. Takano, T. Tsuji, and T. Tanida, *Can. J. Chem.*, **42**, 926 (1964).

(10) We are indebted to K. Morita and J. C. Kauer for samples of the unsubstituted and 4-fluoro derivatives, respectively.

(1) (a) R. Kellogg, *J. Chem. Phys.*, **44**, 411 (1966); (b) R. G. Bennett and P. J. McCartin, *ibid.*, **44**, 1969 (1966).

(2) R. S. H. Liu, *J. Am. Chem. Soc.*, **90**, 215 (1968).

(3) G. S. Hammond, N. J. Turro, and A. Fischer, *ibid.*, **83**, 4674 (1961).

(4) J. R. Edman, *ibid.*, **88**, 3454 (1966).

(5) (a) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Am. Chem. Soc.*, **86**, 3107 (1964); (b) R. S. H. Liu, N. J. Turro, and

Table I. Quantum Yields of Rearrangement of Compounds **1**, **2**, **3**, and **4** with Different Sensitizers[a]

Sensitizer	E_{T_1}, kcal/mole	Quantum yield of reaction[g,h]			
		1	**2**	**3**	**4**
Xanthone	74.2[b]	+	0.17	+	+
Acetophenone	73.6[b]		0.16	0.26	0.49
Benzophenone	68.5[b]	1.03	–	0.18	0.04
2-Acetonaphthone	59.3[b]	3.7×10^{-2}			–
9-Fluorenone	51[b,c]	$<1 \times 10^{-4}$		–	–
Anthracene[f]	42.5[d,e]	+	+	+	+
9,10-Dibromo-An[f]	40.2[e]	8.1×10^{-3}	–	+	+
9,10-Dichloro-An	40.2[e]	3.5×10^{-3}			+
9,10-Dimethyl-An	?	5.9×10^{-4}			
9-Bromo-10-methyl-An	?	6.8×10^{-3}		+	

[a] Degassed solutions, irradiated in the "merry-go-round" apparatus, with Hanovia Hg lamp and Corning 7-60, 0-52 filter plates, transmitting light mainly between 3500 and 3700 Å. [b] See W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 4573 (1964). [c] See K. Yoshikars and D. R. Kearns, *J. Chem. Phys.*, **45**, 1991 (1966). [d] See ref 1a. [e] See S. P. McGlynn, T. Azumi, and M. Kasha, *ibid.*, **40**, 507 (1964). [f] See ref 9. [g] Concentration of **1** = 1.91×10^{-2} *M*. [h] Values not corrected for intersystem crossing efficiencies of sensitizers.

will not provide low-energy pathways of excitation in these molecules.

The quantum yields[7] for the rearrangement of **1** with different sensitizers are shown in Table I. The results for **1** for high-energy sensitizers are consistent with the view that its triplet-state energy is between 59 and 68 kcal/mole so that the rate of transfer, reflected in the quantum yield, is efficient with xanthone and benzophenone, significantly less efficient with 2-acetonaphthone, and insignificant with 9-fluorenone. When the anthracenes,[9] in spite of a further large decrease in T_1 energy, are effective in sensitizing the reaction, it becomes obvious that an explanation involving activated energy transfer is not applicable.[5c,10] Four alternative explanations come to mind: first, the "nonvertical" excitation process with energy transfer from T_1 of anthracene and simultaneous rearrangement of **1**; second, the rearrangement originates from interaction of the anthracene singlet (S_1) with **1**; third, complex formation; and fourth, energy transfer from T_2 of anthracene. We strongly favor the last explanation because of the following observations.

An *n*-hexane solution of **1** (3.33×10^{-2} *M*), 9-fluorenone (1.67×10^{-2} *M*), and 9,10-dibromoanthracene (6.67×10^{-4} *M*) was irradiated with 3600-Å light. At these concentrations, approximately 80% of the incident light is absorbed by fluorenone and 20% by dibromoanthracene. Since the T_1 of fluorenone lies below that of **1** (see above) but higher than the T_1 of dibromoanthracene, *selective excitation of the T_1 state of dibromoanthracene is partially achieved by energy transfer.* Since the efficiency of intersystem crossing in fluorenone[11] (0.93) is higher than that of dibromoanthracene (<0.9),[12] the presence of fluorenone should increase the number of dibromoanthracene T_1 triplets, and the efficiency of the rearrangement of **1** should increase, if a nonvertical excitation process is involved. When the sample was irradiated long enough to produce a 5% conversion of **1** in an identical sample without fluorenone, *no significant amount of rearrangement of* **1** *could be detected.*[13] This result rules out the T_1 of anthracene in the sensitized reaction.

The reaction probably does not result from interaction of anthracene S_1 with **1** because of the observation that quantum yields of the reaction for dibromo-, dichloro-, and dimethylanthracenes (Table I) correspond inversely with fluorescence yields (<0.10,[12] 0.56,[1b] 0.81,[14] respectively) of the anthracenes. Furthermore, the fluorescence lifetime of anthracene is not affected by norbornadiene (**3**) in concentrations as high as 9.0×10^{-1} *M*. The rearrangement probably is also not a consequence of excited- or ground-state complex formation because the absorptions of anthracene solutions did not change when **1** was added, and the efficiency of reaction remained constant with a fivefold change in dibromoanthracene concentrations.

Energy transfer from T_2 remains the only plausible explanation. Since the bimolecular transfer is expected to compete with the fast, internal conversion process, the quantum yield of the reaction should depend on the concentration of the acceptor. The results of such a study are shown in Figure 2. The linear dependence of the reciprocal of quantum yield upon the reciprocal of the average concentration of the acceptor is predicted by the following mechanism.

$$\text{anthracene } (A_{S_0}) \xrightarrow{h\nu} A_{S_1}$$

$$A_{S_1} \longrightarrow A_{T_2} \qquad \text{efficiency} = a$$

$$A_{T_2} \xrightarrow{k_{ic}} A_{T_1} \longrightarrow A_{S_0}$$

$$A_{T_2} + \mathbf{1} \xrightarrow{k_t} A_{S_0} + \mathbf{1}_{T_1}$$

$$\mathbf{1}_{T_1} \longrightarrow \text{product} \qquad \text{efficiency} = b$$

$$\frac{1}{\phi} = \frac{1}{ab}\left(1 + \frac{k_{ic}}{k_t}\frac{1}{[\mathbf{1}]}\right)$$

The value of k_{ic}/k_t calculated from the slope and the intercept of the plot is 2.4, which limits k_{ic}, the rate constant of internal conversion from T_2 to T_1, to 5×10^{10} sec^{-1} (assuming k_t has a maximum value of 2×10^{10}

G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 3406 (1965); (c) W. G. Herkstroeter and G. S. Hammond, *ibid.*, **88**, 4789 (1966); (d) A. Cox, P. de Mayo, and R. W. Yip, *ibid.*, **88**, 1043 (1966); (e) W. Dillion, *ibid.*, **89**, 2742 (1967).

(6) (a) G. S. Hammond, O. Wyatt, C. D. DeBoer, and N. J. Turro, *ibid.*, **86**, 2532 (1964); (b) J. R. Fox and G. S. Hammond, *ibid.*, **86**, 4031 (1964); (c) C. Walling and M. J. Gibian, *ibid.*, **87**, 3413 (1965).

(7) The photosensitized rearrangement of myrcene[8] and the benzophenone–benzhydrol system were used as actinometers.

(8) R. S. H. Liu and G. S. Hammond, *J. Am. Chem. Soc.*, **89**, 4936 (1967).

(9) The rapid dimerization reaction of anthracene precludes quantitative studies for the parent molecule. The T_2 states of 9,10-dichloro- and 9,10-dibromoanthracene are not presently known.

(10) K. Sanders and K. J. L. Bäckström, *Acta Chem. Scand.*, **16**, 958 (1962).

(11) A. A. Lamola and G. S. Hammond, *ibid.*, **43**, 2129 (1965).

(12) W. H. Melhuish, *J. Phys. Chem.*, **65**, 229 (1961).

(13) The reduced efficiency is probably assisted by quenching of the T_2 state of anthracene and possibly T_1 of **1** by fluorenone.

(14) E. J. Bowen, *Advan. Photochem.*, **1**, 32 (1963).

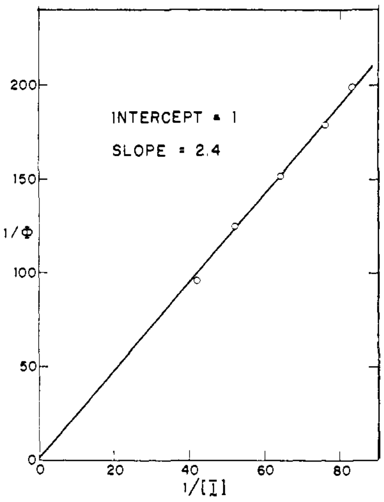

Figure 2. A Stern–Volmer plot of the 9,10-dibromoanthracene-sensitized reaction of **1**.

mole^{-1} sec^{-1}, the calculated diffusion rate constant in hexane at 20°).[15] The average lifetime of the T_2 state of 9,10-dibromoanthracene is, therefore, 2×10^{-11} sec.

Although the present evidence does not rule out completely "relay" mechanisms, suggested by Schenck[16] for other systems, our results require a relay mechanism involving a state other than T_1 and S_1.

From Table I it is obvious that parallel arguments can be presented for compounds **2**, **3**, and **4**, with the proviso that their corresponding triplet-state energies are higher than that of **1**. These systems, however, confirm that in **1** we are not observing an isolated effect. Studies have been expanded to less rigid molecules, where nonvertical excitations are more likely to occur. The results will be reported in the future.

Acknowledgment. The authors wish to thank Drs. R. Kellogg, R. G. Bennett, and H. E. Simmons of Du Pont and Professor G. S. Hammond of California Institute of Technology for helpful discussions and critical comments.

(15) F. Wilkinson, *Advan. Photochem.*, **3**, 248 (1964).

(16) G. O. Schenck and R. Steinmetz, *Bull. Soc. Chim. Belges*, **71**, 781 (1962).

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2,3-Bis(perfluoromethyl)bicyclo[2.2.2]octa-2,5,7-trienes and Their Photorearrangement Reactions

Sir:

The thermal 1,4 cycloaddition of perfluoro-2-butyne to aromatic compounds was reported by Krespan, *et al.*[1] Successful examples of addition to simple benzenoid rings, however, were limited to durene. We wish now to report the isolation of other 1,4 adducts and their photosensitized reactions.

When a mixture of benzene (220 ml) and perfluorobutyne (40.5 g) was heated in a 400-ml high-pressure shaker tube at 180° under autogenous pressure, a gradual decrease of pressure was noticed; after 20 hr a mixture of products was obtained. Glpc analysis of the mixture and comparison of retention times showed, in addition to the previously reported volatile products, 1,1,1,4,4,4-hexafluoro-2-butene, 1,2-bis(perfluoromethyl)benzene, and 1,2,5,6-tetrakis(perfluoromethyl)benzene, the presence of one additional major product. After fractional distillation and glpc separation, the product was isolated in 8% yield.

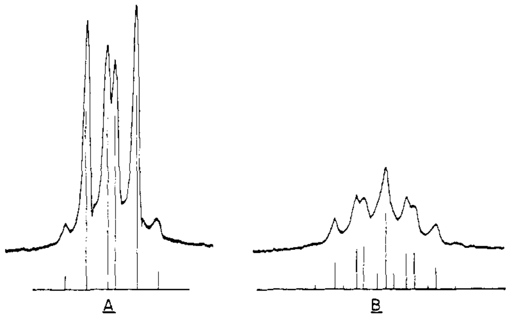
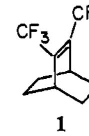


Figure 1. Observed (upper) and calculated (lower) 100-Mc ^{1}H nmr spectrum of bis(perfluoromethyl)bicyclooctatriene.

The compound is a colorless liquid, $\lambda_{\max}^{n\text{-hexane}}$ 262 mμ (ε 144), 220 mμ (sh) (ε 278). Based on the following evidence, it has been assigned the structure 2,3-bis(perfluoromethyl)bicyclo[2.2.2]octa-2,5,7-triene. Results of elemental analysis and molecular weight determination show that the compound is a 1 : 1 adduct. The 100-Mc ^{1}H nmr spectrum[2] (Figure 1) shows two groups of signals centered at 685 (A) and 504 cps (B) with relative intensities of 2 : 4. The 56.4-Mc ^{19}F nmr spectrum shows only a singlet at 3545 cps from Freon 11.[2] On hydrogenation over Pd–charcoal, the compound absorbed 2 moles of hydrogen, giving a product (**1**)



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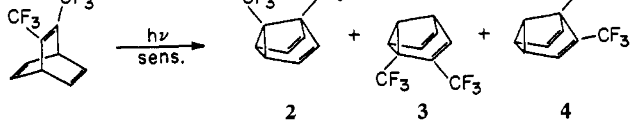
identical (ir, nmr) with the hydrogenation product obtained from reaction of 1,3-cyclohexadiene and perfluorobutyne.

The assignment is further supported by the calculated proton spectrum of **1b** (Figure 1, lower) using the following parameters:[3] $J_{1,2}$ = 5.8 cps, $J_{2,3}$ = 6.2 cps, $J_{1,3}$ = 1.7 cps, $\delta(H_1,H_2)$ = 174.1 cps. The agreement is obviously good.

Corresponding adducts were also obtained from the reaction of toluene and *o*-, *m*-, and *p*-xylenes with perfluorobutyne (Table I). Structural assignments of the products were mainly based on spectroscopic data.

When irradiated with a photosensitizer (acetophenone, benzophenone, or triphenylene), bis(perfluoromethyl)bicyclo[2.2.2]octatriene undergoes a facile rearrangement to give three products, **2–4**. With benzophenone as sensitizer, **2**, **3**, and **4** are formed in relative



2 **3** **4**

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(1) C. G. Krespan, B. C. McKusick, and T. L. Cairns, *J. Am. Chem. Soc.*, **83**, 3428 (1961).

(2) All nmr spectra were taken in CCl$_4$, tetramethylsilane, and Freon 11 as internal standard.

(3) The calculation was based on the assumption that the H–F couplings are zero. Judging by the width of the absorption peaks, this assumption may not be entirely valid.