VOLUME 114, NUMBER 10
MAY 6, 1992

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Direct Observation, Reactions under Matrix-Isolation Conditions, and ab Initio Calculations for Halo(trifluoromethyl)carbenes. Evidence for the Photochemical Addition of a Carbene to Dinitrogen

John E. O'Gara and William P. Dailey*

Contribution from the Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323.
Received December 1, 1989.
Revised Manuscript Received December 27, 1991

Abstract: Photolysis of 3-halo-3-(trifluoromethyl)diazirines (X = F (**4**), Cl (**5**), Br (**6**)) in an argon matrix at 12 K generates the respective singlet halo(trifluoromethyl)carbenes **1**–**3** which were characterized by infrared and ultraviolet spectroscopies and chemical trapping with HCl. Ab initio calculations indicate that all three carbenes should have singlet ground states, consistent with the experimental results. The vibrational spectrum for each carbene was determined using ab initio molecular orbital calculations and after appropriate scaling was in reasonable agreement with the experimentally determined one. The UV spectra calculated for the singlet carbenes using the configuration interaction with single excitations method gave excellent agreement with the experimental results. Extended photolysis ($\lambda > 280$ nm) converts the carbenes to the respective alkenes. A nitrogen matrix gives identical results for **1** and **2**, but **3** was found to add nitrogen photochemically to form the corresponding diazo compound.

While ground-state singlet alkylhalocarbenes can be trapped intermolecularly[1] and observed indirectly by laser flash photolysis in solution,[2] they have proven difficult to observe under low-temperature matrix-isolation conditions. Instead, the carbenes undergo facile hydrogen or alkyl migrations to form alkenes.[3] One recent exception is the successful matrix-isolation and direct laser flash photolytic study of cyclopropylchlorocarbene.[4] Fluorine is very resistant to 1,2-migrations in carbenes, and on the basis of the successful intermolecular chemistry reported earlier for them,[5] we surmised that halo(trifluoromethyl)carbenes would be observable under matrix-isolation conditions. Herein we report the successful generation, observation and reactions under matrix-isolation conditions, and ab initio calculations for fluoro(trifluoromethyl)carbene (**1**), chloro(trifluoromethyl)carbene (**2**), and bromo(trifluoromethyl)carbene (**3**). These are the first alkylbromo- and alkylfluorocarbenes to be observed under these conditions. In addition, we report the novel photochemical addition of nitrogen to a carbene.

Results and Discussion

Generation and Characterization of Halo(trifluoromethyl)carbenes in Argon Matrices. The precursors for halo(trifluoromethyl)carbenes **1**–**3** were the corresponding diazirines **4**–**6**.[5]

---

[1] (a) Moss, R. A.; Munjal, R. C. *J. Chem. Soc., Chem. Commun.* **1978**, 775. (b) Moss, R. A. *Acc. Chem. Res.* **1980**, *13*, 58.

[2] (a) Soundararajan, N.; Platz, M. S.; Jackson, J. E.; Doyle, M. P.; Oon, S.-M.; Liu, M. T. H.; Anand, S. M. *J. Am. Chem. Soc.* **1988**, *110*, 7143. (b) Liu, M. T. H.; Bonneau, R. *J. Am. Chem. Soc.* **1989**, *111*, 6873. (c) Jackson, J. E.; Soundararajan, N.; White, W.; Liu, M. T. H.; Bonneau, R.; Platz, M. S. *J. Am. Chem. Soc.* **1989**, *111*, 6874.

[3] Schaefer, H. F., III. *Acc. Chem. Res.* **1979**, *12*, 288.

[4] (a) Ho, G.-J.; Krogh-Jespersen, K.; Moss, R. A.; Shen, S.; Sheridan, R. S.; Subramanian, R. *J. Am. Chem. Soc.* **1989**, *111*, 6875. (b) Liu, M. T. H.; Bonneau, R. *J. Phys. Chem.* **1989**, *93*, 7298. (c) Moss, R. A.; Ho, G.-J.; Krogh-Jespersen, K. J. *J. Am. Chem. Soc.* **1990**, *112*, 1638.

[5] (a) Grayston, M. W.; Lemal, D. M. *J. Am. Chem. Soc.* **1976**, *98*, 1278. (b) Dailey, W. P. *Tetrahedron Lett.* **1987**, *28*, 5801. (c) Moss, R. A.; Guo, W.; Denney, D. Z.; Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* **1981**, *103*, 6164.

0002-7863/92/1514-3581$03.00/0

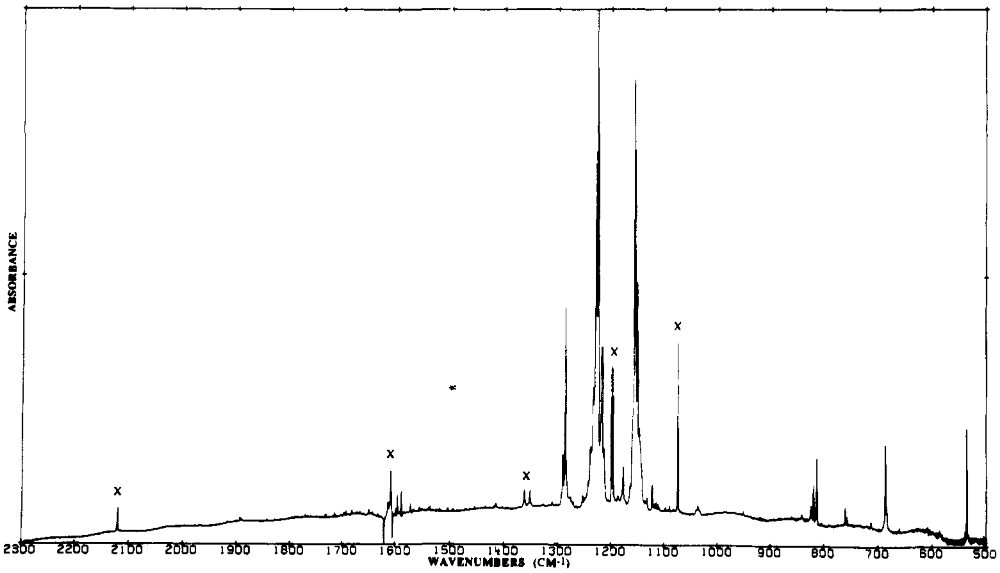


Figure 1. IR spectrum of fluoro(trifluoromethyl)carbene (**1**) in an argon matrix at 12 K. Bands marked with an X are impurities.

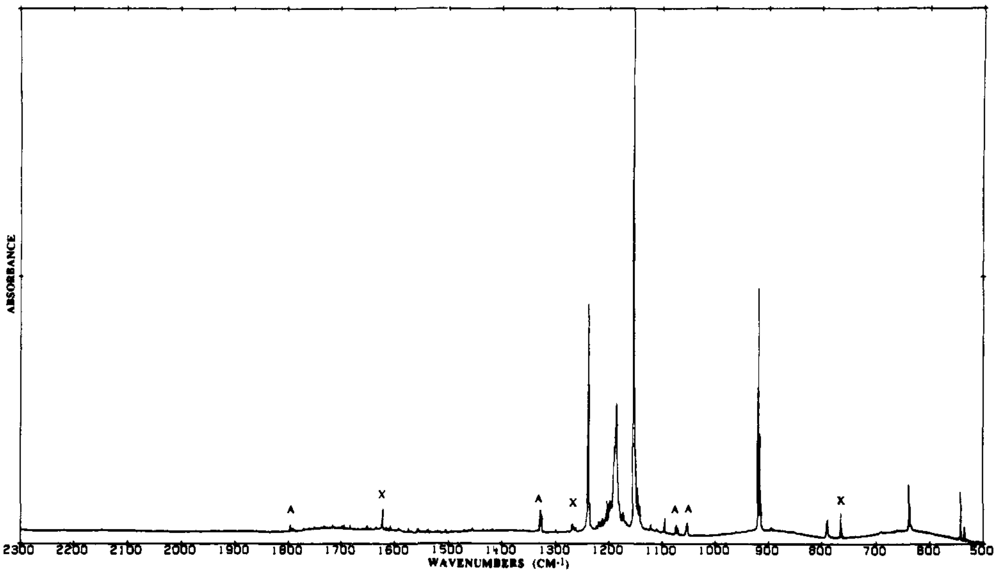


Figure 2. IR spectrum of chloro(trifluoromethyl)carbene (**2**) in an argon matrix at 12 K. Bands marked with an X and A are impurities and chlorotrifluoroethene, respectively.

3-Chloro- and 3-bromo-3-(trifluoromethyl)diazirine (**5** and **6**) were prepared by the Graham oxidation of trifluoroacetamidine using hypochlorite or sodium bromide doped hypochlorite solutions, respectively. 3-Fluoro-3-(trifluoromethyl)diazirine (**4**) was prepared using the Moss "diazirine exchange reaction"[6] of 3-bromo-3-(trifluoromethyl)diazirine with fluoride ion. We note that our studies[7] as well as those reported independently by Creary and Sky[8] suggest that the "diazirine exchange reaction" of halodiazirines most likely proceeds via a double S_N2' or addition–elimination mechanism rather than the diazirinium cation as was originally proposed.[9]

The diazirines, each in turn, were deposited as dilute argon solutions onto a cesium iodide salt plate held at 23 K. Monochromatic irradiation ($\lambda = 320 \pm 10$ nm) of the argon matrix of **4**, **5**, or **6** at 12 K lead to the rapid disappearance of the diazirine IR bands and produced bands that we attribute to the respective carbenes. For instance, irradiation of an argon matrix of 3-fluoro-3-(trifluoromethyl)diazirine (**4**) produced a bright yellow matrix and gave the IR spectrum in Figure 1. Irradiation of an argon matrix of 3-chloro-3-(trifluoromethyl)diazirine (**5**) gave a blue-green matrix and the IR spectrum in Figure 2. Similar irradiation of an argon matrix of 3-bromo-3-(trifluoromethyl)-diazirine (**6**) gave a blue matrix and the IR spectrum in Figure 3. These IR spectra as well as the colors of the matrices were stable for at least several days under the reaction conditions. The major bands in the spectra depicted in Figures 1–3 are assigned to carbenes **1**–**3**, respectively. In all three spectra there are small amounts of impurities which are noted by an X. The major impurity in Figure 1, with bands at 1200 and 1075 cm^{-1}, is due

Table I. Observed IR Spectra of Halo(trifluoromethyl)carbenes in Argon Matrices at 12 K (cm^{-1})

1		**2**		**3**	
freq	rel intens	freq	rel intens	freq	rel intens
1286.6	16	1238.7	43	1229.3	61
1226.4	100	1186.6	62	1178.0	59
1156.9	46	1154.8	100	1147.6	100
1152.6	26	920.0	27	858.3	17
815.1	3	791.7	4	745.2	14
688.3	6	640.3	5	626.1	7
537.4	3	543.6	2	544.1	2
		536.7	1	523.6	2

---

(6) Moss, R. A. In *Chemistry of Diazirines*; Liu, M. T. H., Ed.; CRC Press: Boca Raton, FL, 1987.

(7) Bainbridge, K. E.; Dailey, W. P. *Tetrahedron Lett.* **1989**, *30*, 4901.

(8) Creary, X.; Sky, A. F. *J. Am. Chem. Soc.* **1990**, *112*, 368.

(9) Moss, R. A.; Terpinski, J.; Cox, D. P.; Denney, D. Z.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1985**, *107*, 2743.

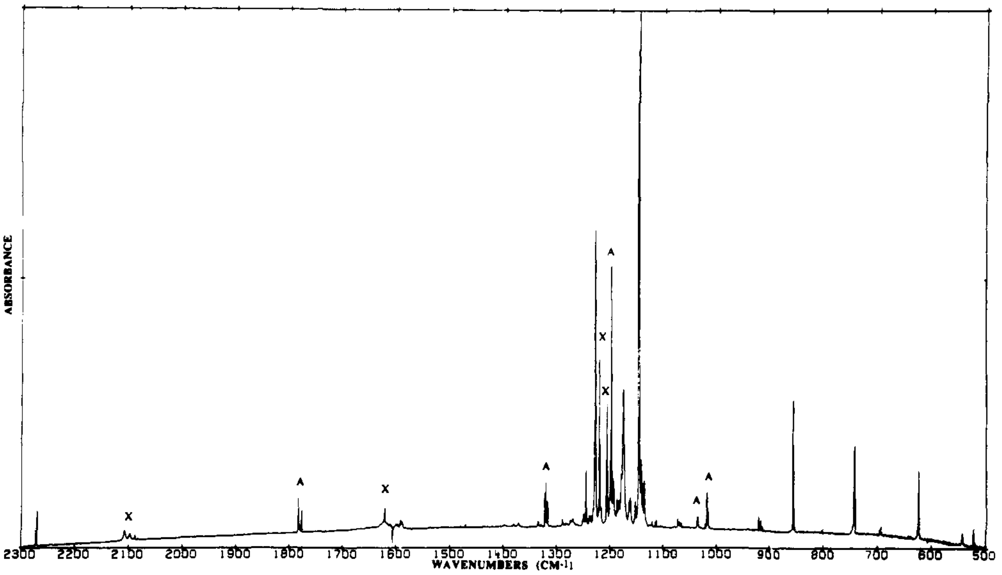
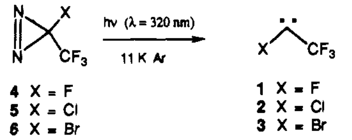
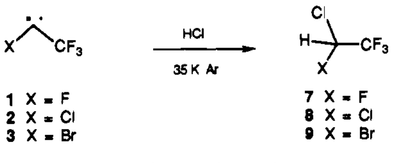


Figure 3. IR spectrum of bromo(trifluoromethyl)carbene (3) in an argon matrix at 12 K. Bands marked with an X and A are impurities and bromotrifluoroethene, respectively.

to bromotrifluoromethane, a byproduct formed during the synthesis of **4**. In Figures 2 and 3, small amounts of the corresponding alkenes (noted by an A) are also present. The alkenes are formed by fluorine atom migration in carbenes **2** and **3**. A compilation of the IR bands assigned to each of the three carbenes is given in Table I.



Chemical evidence for the structures of these carbenes comes from trapping studies with HCl. A mixture of argon/HCl/diazirine (1650:4:1) was deposited onto a cesium iodide salt plate held at 23 K as before. Irradiation of this matrix produced the same bands that we assign to the respective carbenes in addition to a small amount of the corresponding HCl insertion products. If these matrices are allowed to warm to 38 K for several hours, the bands assigned to the respective carbenes disappear and the bands of the known HCl insertion products **7**,[10] **8**,[11] and **9**[12] appear. In the case of carbene **1**, dimerization to a mixture of the known *cis*- and *trans*-octafluoro-2-butenes[13] is a minor side reaction. These trapping studies are good evidence that the carbenes have been formed. Further evidence comes from the photochemical conversion of the carbenes to the corresponding halotrifluoroethenes (see below).



UV Spectra. Evidence in favor of the singlet nature of carbenes **1**–**3** comes from matrix-isolated ultraviolet spectra.[14] The UV spectra for the three carbenes are shown in Figure 4. Carbene **1** had λ_{max} = 465 (ϵ = 100 (L cm^{-1})/mol) and 235 nm,[15] carbene **2** had λ_{max} = 640 (ϵ = 60 (L cm^{-1})/mol) and 235 nm, and carbene **3** had λ_{max} = 665 (ϵ = 45 (L cm^{-1})/mol), 270 (sh), and 235 nm. During the formation of **3** by monochromatic irradiation of **6** at

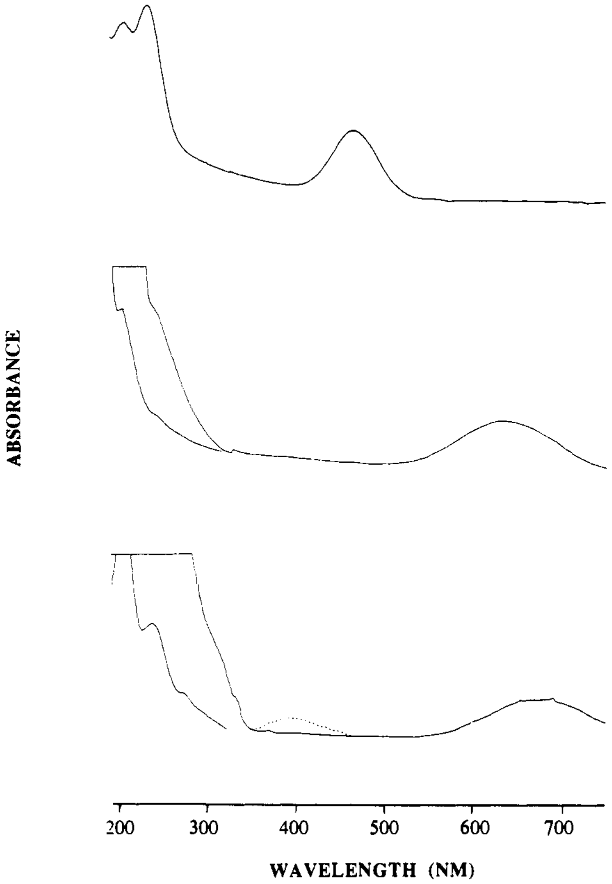


Figure 4. Matrix-isolated UV spectra (Ar, 12 K) of fluoro(trifluoromethyl)carbene (**1**) (upper), chloro(trifluoromethyl)carbene (**2**) (middle), and bromo(trifluoromethyl)carbene (**3**) (lower). Inset below 300 nm in the middle spectrum is times 20%, and inset below 300 nm in lower spectrum is times 10%. The dashed portion of the bottom spectrum is the section which is bleached by brief irradiation at 400 nm and assumed to be a very minor impurity (see text for details).

---

(10) Goldwhite, H.; Haszeldine, R. N.; Mukherjee, R. N. *J. Chem. Soc.* **1961**, 3825.

(11) Nielsen, J. R.; Liang, C. Y.; Smith, D. C. *J. Chem. Phys.* **1953**, *21*, 1060.

(12) Theimer, R.; Nielsen, J. R. *J. Chem. Phys.* **1957**, *27*, 887.

(13) Heicklen, J.; Wachi, F.; Knight, V. *J. Phys. Chem.* **1965**, *69*, 693.

(14) For recent reviews of absorption spectra of carbenes, see: (a) Li, Y.-Z.; Schuster, G. B. In *Handbook of Organic Photochemistry*; Scaiano, J. C., Ed.; CRC Press: Boca Raton, FL, 1989. (b) Zuev, P. S.; Nefedov, O. M. *Russ. Chem. Rev.* **1989**, *58*, 636.

(15) The UV spectrum of **1**, purportedly generated during adiabatic compression of tetrafluoroethylene, is reported to have an absorption at 248.3 nm. See: Kolbanovskii, Y. A. *Russ. Chem. Rev.* **1989**, *58*, 1024.

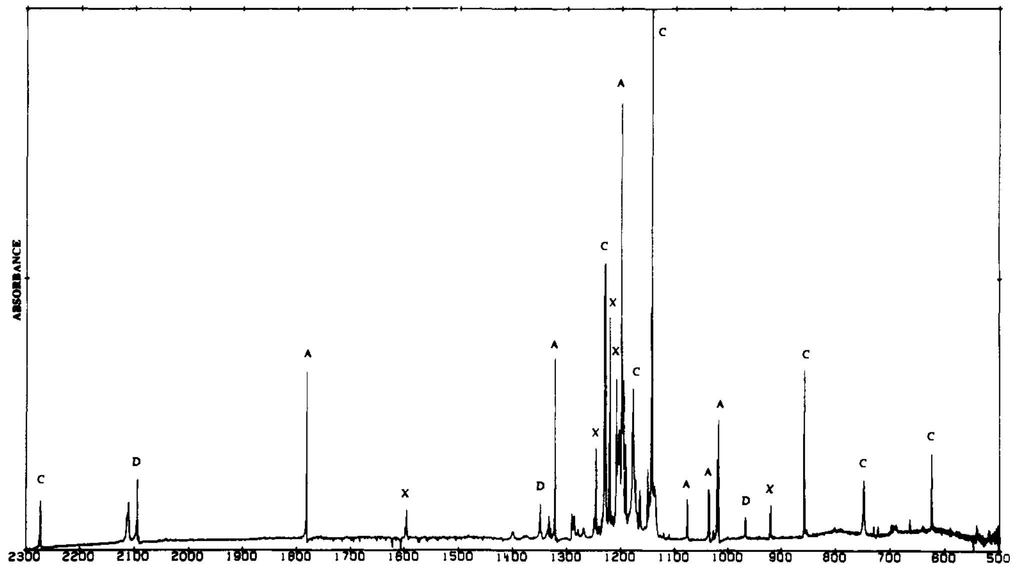
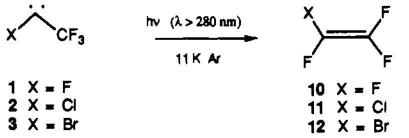


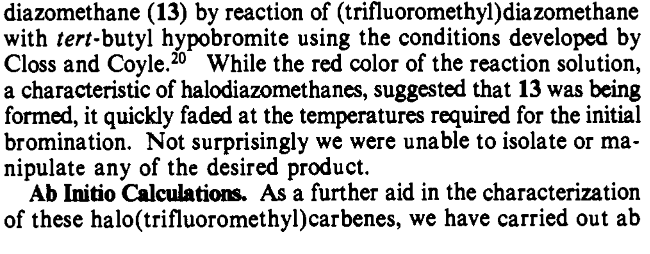
Figure 5. IR spectrum of bromo(trifluoromethyl)carbene (3) in a nitrogen matrix at 12 K obtained by irradiation of 6 at λ = 340 nm. Bands marked with a C, X, A, and D are assigned to carbene 3, impurities, bromotrifluoroethene, and bromo(trifluoromethyl)diazomethane, respectively.

320 nm, there was an additional band present at 400 nm. Very brief irradiation of this matrix at 400 nm led to a bleaching of the 400-nm band with no change in the other UV absorptions. This is shown by the dashed line in Figure 4. Within the limits of our detection, the IR spectrum was unaffected by the photochemical destruction of the 400-nm UV band. We conclude that only a very small impurity was responsible for the band at 400 nm.

In the gas phase, singlet methylene absorbs between 550 and 950 nm, while triplet methylene absorbs at very short wavelengths.[16] The UV results for 1–3 suggest that all three carbenes have singlet ground states. The progression of the longest wavelength λ_{max} ($S_0 \rightarrow S_1$) to shorter wavelengths in the series X = Br, Cl, and F can be attributed to the greater degree of interaction of the heteroatom lone pair with the vacant p orbital of the carbenic carbon.[17] This is also supported by computations (see below). During the formation (or photochemical destruction) of carbenes 1–3, the increase (or decrease) in all of the assigned UV absorptions parallels the gain (or loss) of the IR signals assigned to the respective carbenes. All three carbenes could be photochemically converted to the corresponding halotrifluoroethenes 10–12 using broad-band irradiation (λ > 280 nm), but qualitatively the ease of rearrangement varied with the substituent. Carbene 3 rearranged most easily, followed by carbene 2, and finally carbene 1. In fact carbene 1 was remarkably robust and could survive modest periods of irradiation by the full mercury arc through quartz (λ > 185 nm).



Reactions in Nitrogen Matrices. When nitrogen was used as the matrix material, carbenes 1 and 2 could be generated, observed, and photochemically destroyed in the same manner as in an argon matrix. However, a nitrogen matrix containing bromocarbene 3 revealed some remarkable differences. Photolysis of the bromodiazirine 6 using monochromatic irradiation (λ = 340 nm) produced bands that we assign to the carbene 3 as well as bands for bromotrifluoroethene and a small amount of new compound (Figure 5). The band at 2100 cm^{-1} suggests that this new compound is bromo(trifluoromethyl)diazomethane (13). Addition of nitrogen to carbenes under matrix-isolation conditions is well known[18] as is the interconversion of diazirines and diazo compounds.[19] Monochromatic irradiation of this matrix at the first absorption band of 3 at 680 nm produced no change in the IR spectrum while broad-band irradiation (λ > 280 nm) led to the decomposition of carbene 3 and an increase in alkene 12 just as is observed in argon matrices. However, monochromatic irradiation of the original nitrogen matrix of 3 at 270 nm led to the disappearance of the carbene bands and an increase in the intensities of the bands due to bromotrifluoroethene (12) and those due to diazo compound 13 as well (Figure 6). Unfortunately, we were unable to assign any of the features of the UV spectrum of this matrix to the diazo compound. However, irradiation of this matrix at 460 nm led to the disappearance of the bands due to diazo compound 13 and the reappearance of the bands due to carbene 3 in addition to larger amounts of alkene 12 (Figure 7). The IR bands that are assigned to the diazo compound 13 occur at 2094, 1350, 1234, 1170, 1137, 969, and 732 cm^{-1}.



We attempted to prepare authentic bromo(trifluoromethyl)diazomethane (13) by reaction of (trifluoromethyl)diazomethane with *tert*-butyl hypobromite using the conditions developed by Closs and Coyle.[20] While the red color of the reaction solution, a characteristic of halodiazomethanes, suggested that 13 was being formed, it quickly faded at the temperatures required for the initial bromination. Not surprisingly we were unable to isolate or manipulate any of the desired product.

Ab Initio Calculations. As a further aid in the characterization of these halo(trifluoromethyl)carbenes, we have carried out ab

---

(16) (a) Herzberg, G. *Proc. R. Soc. London* **1961**, *A262*, 291. (b) Herzberg, G.; Johns, J. W. C. *Proc. R. Soc. London* **1964**, *295*, 107.

(17) The same explanation has been used to rationalize the singlet–triplet gaps in halocarbenes; see: Mueller, P. H.; Rondan, N. G.; Houk, K. N.; Harrison, J. F.; Hooper, D.; Willen, B. H.; Liebman, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 5049.

(18) Brahms, J. C.; Dailey, W. P. *J. Am. Chem. Soc.* **1990**, *112*, 4046.

(19) Sheridan, R. S.; Moss, R. A.; Wilk, B. K.; Shen, S.; Wlostowski, M.; Kesselmayer, M. A.; Subramanian, R.; Kmiecik-Lawrynowicz, G.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1988**, *110*, 7563.

(20) Closs, G. L.; Coyle, J. J. *J. Am. Chem. Soc.* **1965**, *87*, 4270.

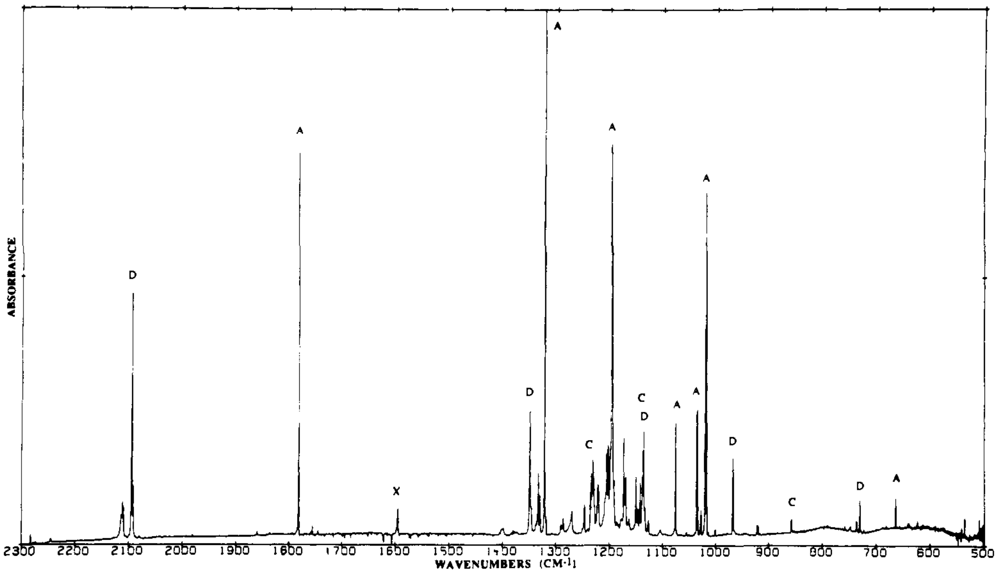


Figure 6. IR spectrum of bromo(trifluoromethyl)diazomethane (**13**) in a nitrogen matrix at 12 K prepared by irradiation of the matrix in Figure 5 at λ = 270 nm. Bands marked with a C, X, A, and D are assigned to carbene **3**, impurities, bromotrifluoroethene, and bromo(trifluoromethyl)diazomethane, respectively.

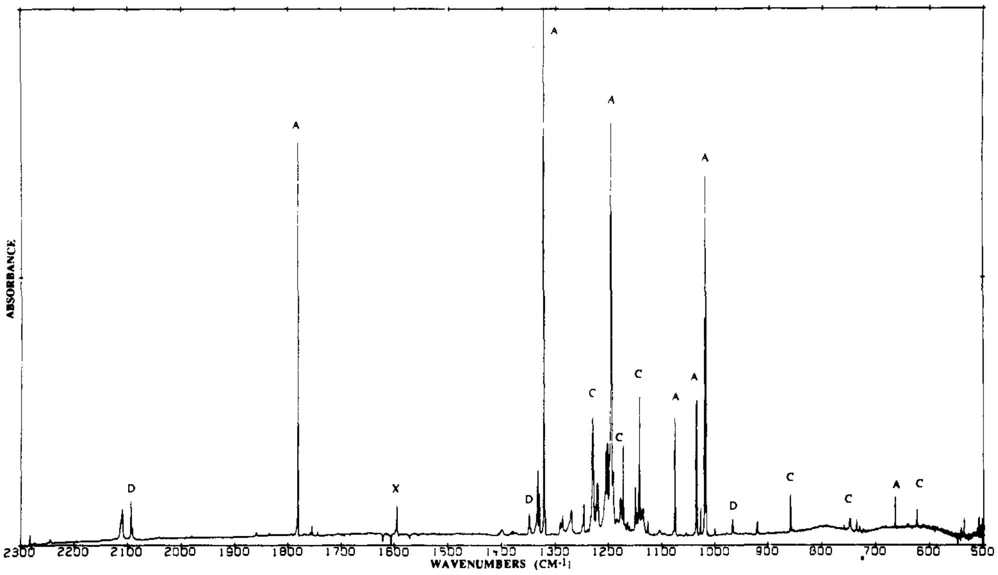


Figure 7. IR spectrum of bromo(trifluoromethyl)carbene (**3**) in a nitrogen matrix at 12 K prepared by irradiation of the matrix in Figure 6 at λ = 450 nm. Bands marked with a C, X, A, and D are assigned to carbene **3**, impurities, bromotrifluoroethene, and bromo(trifluoromethyl)diazomethane, respectively.

initio calculations on the singlet and triplet states of these species. Dixon has reported calculations on a series of trifluoromethyl-substituted carbenes, including fluoro(trifluoromethyl)carbene (**1**), using a double-ζ (DZ) basis set with polarization functions (d orbitals) on the carbon atoms.[21] In this study Dixon noted that replacement of a hydrogen by a trifluoromethyl group had virtually no effect on the singlet–triplet gap of the resulting carbene. For instance, the singlet–triplet gap in (trifluoromethyl)carbene was calculated to be almost exactly the same as that of methylene. The parent halomethylenes have been studied using large basis sets (triple-ζ plus double polarization (TZ+2P)) and various levels of electron correlation.[22] Because of the size of our molecules, it was impossible to carry out similar studies using these large basis sets. Instead we have performed geometry-optimized calculations using the Dunning/Hay double-ζ plus polarization basis set[23] (DZ+P) available in Gaussian 90[24] and GAMESS.[25] The comparable bromine basis set (14s 11p 5d/9s 7p 2d) was taken from the literature.[26] Single-point energy calculations were carried out using these DZ+P basis sets modified to have two sets of polarization functions (a = 1.5 and 0.35) on the carbene carbon. We will designate these basis sets as DZ+P(2P$_c$). Gradient geometry optimizations were carried out using several types of wave functions. For singlet states, both self-consistent field (SCF) and two-configuration SCF (TCSCF) wave functions were employed. For triplet states both the spin-unrestricted SCF (UHF) and spin-restricted SCF (ROHF) methods were employed. Previous researchers have noted that at least a TCSCF wave function is needed to describe the singlet states of carbenes when

---

(21) Dixon, D. A. *J. Phys. Chem.* **1986**, *90*, 54.

(22) Scuseria, G. E.; Durân, M.; Maclagan, R. G. A. R.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1986**, *108*, 3248.

(23) Dunning, T. H.; Hay, P. J. In *Methods of Electronic Structure Theory*; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977.

(24) Gaussian 90, Revision H: Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A., Gaussian, Inc., Pittsburgh, PA, 1990.

(25) GAMESS: Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Jensen, J. H.; Koseki, S.; Gordon, M. S.; Nguyen, K. A.; Windus, T. L.; Elbert, S. T. *QCPE Bull.* **1990**, *10*, 52.

(26) Bauschlicher, C. W., Jr.; Schaefer, H. F., III; Bagus, P. S. *J. Am. Chem. Soc.* **1977**, *99*, 7106.

Table II. Geometries and Energies of Halocarbenes Determined Using TCSCF/ROHF ab Initio Calculations[a]

		basis set[b]	−*E*	rel *E*	*r*(C–H)	*r*(C–X)	*θ*(H–C–X)
HCF	$^1A'$	DZ+P	137.81431	0.0	1.107	1.304	103.1
		DZ+P(2P$_c$)	137.81848	0.0			
		TZ+2P	137.83580	0.0	1.104	1.294	103.3
	$^3A''$	DZ+P	137.80106	8.3	1.076	1.313	121.0
		DZ+P(2P$_c$)	137.80252	10.0			
		TZ+2P	137.82009	9.9	1.073	1.304	121.1
HCCl	$^1A'$	DZ+P	497.81832	1.0	1.096	1.718	103.3
		DZ+2P(2P$_c$)	497.82447	0.0			
		TZ+2P	497.86631	0.0	1.092	1.725	102.1
	$^3A''$	DZ+P	497.81985	0.0	1.074	1.695	124.7
		DZ+P(2P$_c$)	497.82092	2.2			
		TZ+2P	497.86298	2.1	1.070	1.699	124.4
HCBr	$^1A'$	DZ+P	2610.66527	3.1	1.095	1.895	102.9
		DZ+P(2P$_c$)	2610.67867	0.0			
		TZ+2P	2610.72546	0.0	1.091	1.884	102.0
	$^3A''$	DZ+P	2610.67024	0.0	1.073	1.851	125.4
		DZ+P(2P$_c$)	2610.67803	0.4			
		TZ+2P	2610.72432	0.7	1.071	1.847	125.1

[a] Bond lengths in angstroms, bond angles in degrees, total energies in hartrees, relative energies in kilocalories per mol. [b] Basis sets are described in the text.

the difference in energy between the singlet and triplet states is desired.[27] Thus, we will use this minimal description of the singlet states together with the ROHF description for the triplets to obtain a measure of the singlet–triplet gaps in the halocarbenes. We will begin by comparing the results of the DZ+P basis with the previous TZ+2P results for fluoromethylene (**14**), chloromethylene (**15**), and bromomethylene (**16**). The results are shown in Table II.

Overall, the structures of **14–16** calculated at the TCSCF/ROHF level using the DZ+P basis set are extremely similar to those calculated with the larger TZ+2P basis set. The bond lengths are very close, varying at most by 0.011 Å. Likewise, the bond angles are predicted to be almost exactly the same using either basis set. We conclude that geometries obtained with the DZ+P basis set will be similar to those obtained with the TZ+2P basis. Compared with the TZ+2P results, however, the relative energies of the singlet and triplet states are quite different using the smaller DZ+P basis set. At the TCSCF/ROHF level, the TZ+2P basis predicts that all three carbenes will have singlet ground states, with the triplet state higher in energy by 9.9, 2.1, and 0.7 kcal/mol for **14**, **15**, and **16**, respectively. With the DZ+P basis, the triplet states are predicted to be 8.3, −1.0, and −3.1 kcal/mol above the singlet state. In other words, both chlorocarbene and bromocarbene are predicted to have triplet ground states with the DZ+P basis. With the DZ+P(2P$_c$) basis, however, the predictions are very similar to those obtained with the TZ+2P basis set. The triplet states are now predicted to be 10.0, 2.2, and 0.4 kcal/mol above the singlet state for **14**, **15**, and **16**, respectively. We note that the present procedure of using single-point energies calculated with the DZ+P(2P$_c$) basis at DZ+P optimized geometries gives values for the singlet–triplet splittings that are very similar to those obtained using the much more expensive TZ+2P basis and geometry optimization. Obtaining more reliable estimates for the singlet–triplet gaps in these compounds requires correlated methods more elaborate than we could expect to apply to the analogous (trifluoromethyl)carbenes. Instead, we will use the difference between the "best" calculated singlet–triplet splittings and our TCSCF/ROHF DZ+P(2P$_c$) results for the halomethylenes **14–16** to empirically correct the results obtained for the halo(trifluoromethyl)carbenes **1–3**. On the basis of Davidson corrected CI calculations with the TZ+2P basis sets, the best theoretical estimates[22] for the singlet–triplet gaps in fluorocarbene, chlorocarbene, and bromocarbene are 13.2, 5.4, and 4.1 kcal/mol, respectively, with the singlet being the ground state for all three. At the TCSCF/ROHF level with the DZ+P(2P$_c$) basis sets, our results are 10.0, 2.2, and 0.4 kcal/mol, respectively. Thus, to obtain realistic values for the singlet–triplet gaps, we will empirically correct the values calculated for the halo(trifluoromethyl)carbenes **1**, **2**, and **3** by 3.2, 3.2, and 3.7 kcal/mol, respectively.

Table III. Geometries for Singlet Halo(trifluoromethyl)carbenes Determined Using ab Initio Calculations with the DZ+P Basis Set[a]

	X = F		X = Cl		X = Br	
	SCF	TCSCF	SCF	TCSCF	SCF	TCSCF
r(C1X)	1.280	1.286	1.684	1.698	1.846	1.861
r(C1C2)	1.549	1.552	1.539	1.543	1.537	1.541
r(C2F1)	1.319	1.318	1.319	1.319	1.319	1.318
r(C2F2)	1.310	1.311	1.312	1.313	1.312	1.312
r(C2F3)	1.316	1.313	1.315	1.314	1.316	1.314
θ(XC1C2)	105.32	105.20	110.10	109.10	111.79	111.35
θ(C1C2F1)	106.66	106.99	106.03	106.97	105.67	105.91
θ(C1C2F2)	109.83	109.61	109.21	109.13	109.09	108.68
θ(C1C2F3)	114.11	114.06	116.53	115.58	117.14	117.22
θ(XC1C2F1)	89.80	89.43	91.84	83.11	93.29	93.08
θ(XC1C2F2)	207.79	207.38	209.09	200.43	210.40	210.02
θ(XC1C2F3)	329.66	329.06	331.04	321.80	332.52	331.97

[a] Distances in angstroms, angles in degrees.

Table IV. Geometries for Triplet Halo(trifluoromethyl)carbenes Determined Using ab Initio Calculations with the DZ+P Basis Set[a]

	X = F		X = Cl		X = Br	
	UHF	ROHF	UHF	ROHF	UHF	ROHF
r(C1X)	1.302	1.301	1.684	1.689	1.836	1.838
r(C1C2)	1.497	1.498	1.495	1.497	1.495	1.496
r(C2F1)	1.314	1.314	1.316	1.315	1.316	1.315
r(C2F2)	1.318	1.318	1.319	1.319	1.319	1.318
r(C2F3)	1.318	1.318	1.319	1.319	1.319	1.318
θ(XC1C2)	120.75	120.48	126.09	125.06	128.16	127.15
θ(C1C2F1)	109.11	108.99	109.46	109.15	109.58	109.16
θ(C1C2F2)	111.66	111.70	111.83	111.89	111.84	111.97
θ(C1C2F3)	111.66	111.70	111.83	111.89	111.84	111.97
θ(XC1C2F1)	180.00	180.00	180.00	180.00	180.00	180.00
θ(XC1C2F2)	60.10	60.12	60.21	60.24	60.19	60.28
θ(XC1C2F3)	299.9	299.89	299.79	299.76	299.81	299.72

[a] Distances in angstroms, angles in degrees.

The calculated structures for singlet and triplet halo(trifluoromethyl)carbenes **1–3** are shown in Tables III and IV, respectively. The total energies are given in Table V. In general, the geometries of the singlet carbenes calculated at the SCF or TCSCF level are very similar. The only notable differences in the structures of the singlet carbenes calculated by the two methods are the C–X bond lengths which are calculated to be 0.006–0.025 Å longer using the TCSCF method. Because of the highly electronegative trifluoromethyl group, the C–X bond distances are calculated to be 0.018–0.034 Å shorter in singlet **1–3** compared to the corresponding singlet halomethylenes **14–16**. Comparison of the bond angle about the carbene carbon in the halo(tri-

---

[27] Bender, C. F.; Schaefer, H. F., III; Franceschetti, D. R.; Allen, L. C. *J. Am. Chem. Soc.* **1972**, *94*, 6888.

Table V. Calculated Energies (hartrees) of Halo(trifluoromethyl)carbenes Using ab Initio Calculations

molecule	state	method/basis	energy	rel E^a
$FCCF_3$ (**1**)	S	SCF/DZ+P	−473.503 18	
	S	TCSCF/DZ+P	−473.524 32	
	S	TCSCF/DZ+P(2P$_c$)	−473.528 04	0.0
	T	UHF/DZ+P	−473.513 54	
	T	ROHF/DZ+P	−473.508 85	
	T	ROHF/DZ+P(2P$_c$)	−473.511 28	10.5
$ClCCF_3$ (**2**)	S	SCF/DZ+P	−833.502 55	
	S	TCSCF/DZ+P	−833.523 13	
	S	TCSCF/DZ+P(2P$_c$)	−833.528 40	0.0
	T	UHF/DZ+P	−833.533 15	
	T	ROHF/DZ+P	−833.526 77	
	T	ROHF/DZ+P(2P$_c$)	−833.528 41	0.0
$BrCCF_3$ (**3**)	S	SCF/DZ+P	−2946.347 85	
	S	TCSCF/DZ+P	−2946.368 11	
	S	TCSCF/DZ+P(2P$_c$)	−2946.381 15	0.0
	T	UHF/DZ+P	−2946.383 90	
	T	ROHF/DZ+P	−2946.378 07	
	T	ROHF/DZ+P(2P$_c$)	−2946.386 22	−3.2

[a] Values in kilocalories per mole.

fluoromethyl)carbenes with that in the corresponding halomethylenes reveals an interesting trend. In all the singlet halomethylenes **14–16**, the XCH angle is calculated to be very close to 103°. In singlet **1** the FCC angle is calculated to be slightly wider, 105°, while in both singlet **2** and **3** the XCC angles are predicted to be even larger, 109° and 111°, respectively. The widening of the XCC angle is due to steric interactions between the trifluoromethyl group and the halogen atom. In the triplet halomethylenes **14–16**, the XCH angle is calculated to be between 121° and 125°. The XCC angle in the triplet halo(trifluoromethyl)carbenes **1–3** is in a similar range of 120–127°. The larger XCC angle preferred by the triplet states has relieved a major portion of the steric interaction between the trifluoromethyl group and the larger halogen atoms. At the TCSCF/ROHF level of theory with the DZ+P(2P$_c$) basis set, the calculated singlet–triplet gaps for **1**, **2**, and **3** are 10.5, 0.0, and −3.2 kcal/mol, respectively. Applying our empirical corrections yields values of 13.7, 3.2, and 0.5 kcal/mol, respectively. Thus, with these corrections, all three carbenes are predicted to have singlet ground states, consistent with our experimental observations. The value for the singlet–triplet gap in **1** is similar to that predicted for fluoromethylene while the values for **2** and **3** are substantially smaller than the values predicted for chloromethylene and bromomethylene. The steric effect that widens the XCC angle in the singlet states of these compounds serves to destabilize the singlet state relative to the triplet.[28] The similarity in the XCC angles in triplet **1–3** compared with triplet **14–16**, respectively, suggests that the steric interactions in the triplet (trifluoromethyl)carbenes are similar to those in the parent halomethylenes. To determine the magnitude of the destabilization in the singlet states of **2** and **3** due to bond angle deformation, the energies of the singlet states of chloromethylene and bromomethylene were determined with the XCC angles calculated for **2** and **3**. With a ClCH angle of 109°, singlet chlorocarbene is predicted to be 0.9 kcal/mol less stable than the minimum energy structure. Similarly, singlet bromocarbene with a BrCH angle of 111° is predicted to be 1.8 kcal/mol less stable than its minimum energy structure. Thus, a major reason for the decreased singlet–triplet gaps in **2** and **3** compared with the parent methylenes is due to the larger bond angle about the carbene carbon atom which is caused by a steric effect between the trifluoromethyl group and the halogen in the singlet states of these species.

Table VI. Calculated Vibrational Spectrum of Singlet Fluoro(trifluoromethyl)carbene with the DZ+P Basis Set[a]

SCF			TCSCF	
calcd	scaled	intens	calcd	scaled
1496.6	1287	98	1491.4	1282
1419.6	1221	357	1416.1	1218
1377.2	1184	247	1364.9	1174
1348.8	1160	396	1349.0	1160
926.4	834	30	925.9	833
754.8	679	43	752.6	677
595.5	536	12	593.3	534
587.9	529	13	587.5	529
456.3	411	2	453.9	409
363.9	328	11	363.1	327
285.6	257	4	282.7	254
30.2	27	1	26.1	23

[a] Frequencies in inverse centimeters, intensities in kilometers per mole. Bands above 1200 cm^{-1} were scaled by a factor of 0.86, while the remaining bands were scaled by a factor of 0.90. See text for details.

Table VII. Calculated Vibrational Spectrum of Triplet Fluoro(trifluoromethyl)carbene with the DZ+P Basis Set[a]

UHF			ROHF	
calcd	scaled	intens	calcd	scaled
1568.4	1349	84	1566.3	1347
1388.5	1194	348	1392.5	1197
1343.5	1155	376	1347.2	1159
1321.0	1136	335	1323.0	1138
950.3	855	14	953.0	858
744.6	670	37	746.9	672
624.8	562	3	624.3	562
607.2	546	7	607.3	546
461.6	415	1	461.4	415
450.6	405	1	451.5	406
226.8	204	4	226.6	204
83.9	75	2	83.8	75

[a] Frequencies in inverse centimeters, intensities in kilometers per mole. Bands above 1000 cm^{-1} were scaled by a factor of 0.86, while the remaining bands were scaled by a factor of 0.90. See text for details.

Table VIII. Calculated Vibrational Spectrum of Singlet Chloro(trifluoromethyl)carbene with the DZ+P Basis Set[a]

SCF			TCSCF	
calcd	scaled	intens	calcd	scaled
1437.9	1237	197	1442.8	1241
1395.4	1200	312	1396.5	1201
1347.2	1159	376	1348.7	1160
996.9	897	142	982.0	884
878.3	790	42	880.7	793
703.8	633	37	701.9	632
596.4	537	13	594.1	535
583.8	525	10	580.7	523
403.1	363	4	395.2	356
371.0	334	6	356.8	321
246.8	222	2	237.8	214
35.0	31	1	37.0	33

[a] Frequencies in inverse centimeters, intensities in kilometers per mole. Bands above 1200 cm^{-1} were scaled by a factor of 0.86, while the remaining bands were scaled by a factor of 0.90. See text for details.

The vibrational spectra for both the singlet and triplet states of **1–3** were determined analytically at each level of theory. At the RHF and UHF levels the band intensities were also obtained. The results are shown in Tables VI–XI. For each of the three singlet carbenes **1–3**, differences between the calculated frequencies at the RHF and TCSCF levels are small; the largest difference is less than 20 cm^{-1}. Even smaller differences are observed for triplet carbenes **1–3** when the UHF and ROHF calculated frequencies are compared. We note that the much less expensive RHF and UHF methods give frequencies very similar to those obtained with the more expensive TCSCF and ROHF methods.

Comparison of the calculated vibrational frequencies and intensities for each carbene in its singlet and triplet state reveals that there are relatively small differences between them. A reasonable agreement between the predicted frequencies for singlet

---

(28) The same explanation has been used to rationalize the chemistry of dimesitylcarbene. See: Nazran, A. S.; Griller, D. *J. Am. Chem. Soc.* **1984**, *106*, 543 and references therein.

Table IX. Calculated Vibrational Spectrum of Triplet Chloro(trifluoromethyl)carbene with the DZ+P Basis Set[a]

UHF			ROHF	
calcd	scaled	intens	calcd	scaled
1471.2	1265	243	1472.2	1266
1373.5	1181	325	1378.4	1185
1339.3	1152	370	1343.8	1156
1081.5	930	145	1077.9	927
867.6	781	28	873.9	787
712.2	641	21	715.8	644
622.7	560	4	621.8	560
582.8	524	2	584.1	526
453.1	408	1	452.4	407
389.5	350	0	390.9	352
179.0	161	2	181.0	163
71.2	64	0	72.6	65

[a] Frequencies in inverse centimeters intensities in kilometers per mole. Bands above 1000 cm^{-1} were scaled by a factor of 0.86, while the remaining bands were scaled by a factor of 0.90. See text for details.

Table X. Calculated Vibrational Spectrum of Singlet Bromo(trifluoromethyl)carbene with the DZ+P Basis Set[a]

SCF			TCSCF	
calcd	scaled	intens	calcd	scaled
1424.2	1225	263	1427.2	1227
1390.3	1196	279	1390.2	1196
1347.6	1159	381	1349.3	1160
946.1	851	48	939.0	845
793.8	714	95	789.3	710
693.9	625	38	692.6	623
597.3	537	13	596.4	537
564.8	508	15	563.6	507
391.0	352	11	387.1	348
332.5	299	3	329.5	296
203.8	183	1	201.2	181
35.9	32	1	31.1	28

[a] Frequencies in inverse centimeters, intensities in kilometers per mole. Bands above 1200 cm^{-1} were scaled by a factor of 0.86, while the remaining bands were scaled by a factor of 0.90. See text for details.

Table XI. Calculated Vibrational Spectrum of Triplet Bromo(trifluoromethyl)carbene with the DZ+P Basis Set[a]

UHF			ROHF	
calcd	scaled	intens	calcd	scaled
1455.5	1252	327	1457.1	1253
1370.1	1178	315	1373.6	1181
1338.9	1151	380	1342.2	1154
1029.6	885	78	1025.6	882
807.5	727	44	811.2	730
701.6	631	13	706.6	636
622.5	560	5	621.6	559
564.4	508	7	566.6	510
451.3	406	0	450.4	405
333.7	300	0	334.8	301
148.5	134	2	151.2	136
63.5	57	0	64.4	58

[a] Frequencies in inverse centimeters, intensities in kilometers per mole. Bands above 1000 cm^{-1} were scaled by a factor of 0.86, while the remaining bands were scaled by a factor of 0.90. See text for details.

Table XII. Comparison of Calculated (CIS/DZ+P) and Experimental UV Spectra of Singlet Carbenes

carbene	λ_{max}(calcd)	λ_{max}(obs)	carbene	λ_{max}(calcd)	λ_{max}(obs)
CH_2	812	550–950[a]	CCl_2	464	440–500[f]
CHF	477	430–600[b]	$FCCF_3$	445	390–540[g]
CHCl	599	550–820[c]	$ClCCF_3$	608	530–740[g]
CF_2	232	220–270[d]	$BrCCF_3$	680	540–780[g]
CFCl	331	340–390[e]			

[a] Reference 16. [b] Merer, A. J.; Travis, D. N. *Can. J. Phys.* **1966**, *44*, 525. [c] Merer, A. J.; Travis, D. N. *Can. J. Phys.* **1966**, *44*, 1541. [d] Smith, C. E.; Jacox, M. E.; Milligan, D. E. *J. Mol. Spectrosc.* **1976**, *60*, 381. [e] Smith, C. E.; Milligan, D. E.; Jacox, M. E. *J. Chem. Phys.* **1971**, *54*, 2780. [f] Jacox, M. E.; Milligan, D. E. *Chem. Phys.* **1976**, *16*, 195. [g] Present work.

1–3 and the experimentally determined ones occurs if the calculated frequencies above 1200 cm^{-1} are scaled by a factor of 0.86 while the calculated frequencies below this value are scaled by a factor of 0.90. Other researchers have used a similar two-scale factor approach for hydrocarbons where the C–H frequencies are scaled by a factor of 0.91 and the other frequencies are scaled by a factor of 0.88.[29] With these scaling factors the average error between the frequencies calculated for the singlet states of **1–3** and those observed is about 10 cm^{-1}. Almost the same agreement between the frequencies calculated for triplet **1–3** and the experimental values occurs if a scaling factor of 0.86 is used for calculated frequencies above 1000 cm^{-1} and a scaling factor of 0.90 is applied to the remaining ones. The average error between the frequencies calculated for the triplet states of **2** and **3** and those observed is again about 10 cm^{-1}. The error between the scaled frequencies calculated for triplet **1** and the experimental values is substantially larger with an average value of about 25 cm^{-1}. Because of the similarity in the agreement between the experimental and calculated IR frequencies for the singlet and triplet carbenes, no definitive statement about the ground-state multiplicities of carbenes **2** and **3** can be made on this basis. The substantially better agreement between the IR values calculated for the singlet state of **1** and the experimental ones reinforces the conclusion obtained from analysis of the UV spectra that **1** is a ground-state singlet carbene.

The ultraviolet spectra were calculated using the CIS (configuration interaction with single excitations) method available in Gaussian 90. The calculations employed the structures and basis set used to obtain the SCF and UHF results in Tables III and IV and used the fixed-core approximation. The first transition in the UV spectra of singlet carbenes **1**, **2**, and **3** is predicted to occur at 445, 608, and 680 nm, respectively, in excellent agreement with the experimental results. For comparison, the first transition in the UV spectra of the triplet states of **1**, **2**, and **3** is predicted to be at 144, 184, and 214 nm, respectively. Similar CIS calculations using the DZ+P basis set were carried out on the singlet states of several halomethylenes as well as on singlet methylene itself. The results are shown in Table XII and are compared with the experimentally determined values. In general, there is very good agreement, and this strongly suggests that **1–3** do indeed have singlet ground states.

Summary

In conclusion, we have demonstrated that a series of singlet halo(trifluoromethyl)carbenes (**1–3**) can be generated under matrix-isolation conditions from the corresponding 3-halo-3-(trifluoromethyl)diazirines **4–6**. These carbenes can be trapped with HCl to form the corresponding insertion products. Upon irradiation they undergo fluorine atom migration to yield the corresponding ethylene. An analysis of the UV spectra suggests that carbenes **1–3** have singlet ground states. Comparison of the experimental IR spectra with those calculated using ab initio molecular orbital theory do not permit a definitive assignment to singlet or triplet states for **2** and **3**. A substantially better agreement between the scaled calculated frequencies for the singlet state compared with those of the triplet state suggests that **1** is a ground-state singlet carbene. Ab initio calculations combined with empirical corrections predict that all three carbenes should have singlet ground states in agreement with the UV results.

Experimental Section

Matrix-Isolation Experiment. An Air Products Model DE202 Displex closed-cycle helium refrigeration system with standard DMX-1 interface and IR04WSL compressor provided cryogenic temperatures as low as 12 K. The temperature was measured using a 0.07% iron-doped gold vs

---

[29] Wiberg, K. B.; Walters, V. A.; Dailey, W. P. *J. Am. Chem. Soc.* **1985**, *107*, 4860.

chromel thermocouple which was pressed against the spectroscopic window by the holder. Indium served as a thermal gasket between the holder and the window. The thermocouple wires were connected to an Air Products APD-E temperature indicator/controller providing an indicator temperature accuracy of ±0.5 K. This unit operated a 20-W resistive heater which allowed for thermal regulation of the cryostat at preset temperatures.

Deposition mixtures were prepared in a 2.5-L manifold evacuated to 10^{-6} Torr (Varian 843 vacuum ionization gauge). Diazirine was released into the manifold and measured using a Varian 843 thermocouple pressure gauge. The inert medium, argon or nitrogen (Matheson, 99.9995% minimum purity), was then added to the manifold as monitored by a differential pressure gauge (Pennwalt Co., Wallace and Tiernan Division, model 62A-4D-0800). Usual inert gas to diazirine ratios were 1500–3000:1 for IR spectroscopy and 200–1000:1 for UV spectroscopy. The flow rate to the cold finger was controlled by a variable leak valve and measured by the differential pressure gauge. Standard experiments consisted of 100–150 Torr deposited at 2 Torr/min (IR) and 130–250 Torr deposited at 1 Torr/min (UV) for transparent matrices of sufficient concentration for analysis. The cold head was insulated by evacuation of the system to 10^{-6} Torr. The diazirine/inert gas mixtures were then deposited onto a 2.5-cm CsI window at 23 K for IR analysis or a 2.5-cm sapphire window at 26 K for UV analysis. After completion of deposition, the window was cooled to 12 K. The cryostat was sealed from the manifold, and a vacuum was maintained via cryogenic pumping. The vacuum shroud was equipped with four ports. One side had a deposition tube while its opposite side had a quartz window for matrix viewing and short-wavelength photolysis. The remaining two ports contained KBr salt plates for IR spectroscopy or quartz plates for UV spectroscopy.

Monochromatic irradiation of the matrix medium was achieved using a Photon Technologies Inc. Model A 1010 monochromator with a 75-W xenon lamp. A 1200 line/mm grating and 1-cm slit width allowed for effective radiation of ±10 nm from the preselected wavelength. Broad-band irradiation was accomplished using a 450-W medium-pressure Hg vapor lamp in a water-cooled quartz immersion well. Band-pass filters (Pyrex, $\lambda < 280$ nm; Vycor, $\lambda < 220$ nm; Corning 754, $\lambda > 450$ nm; Corning 052, $\lambda < 340$ nm) were also used for various irradiations. For trapping experiments average mixture ratios of diazirine, HCl, and argon were 1:4:1650 which were deposited in the manner described above. Matrices were annealed by raising the window temperature slowly (1 K/10 min) to 38–39 K, at which point the temperature was held until completion of the reaction as observed by FTIR spectroscopy.

IR spectra were recorded on an IBM IR/97 FTIR spectrometer at 0.5-cm^{-1} resolution. The spectra shown were produced by a ratio of the sample beam spectrum against a reference spectrum of pure, matrix-isolated argon under near-identical conditions. UV spectra were recorded on a Perkin-Elmer Lambda 3A UV/vis spectrophotometer and are shown as the single-beam spectra.

Caution: All diazirines are potentially explosive and should be treated with due care.

Matrix Isolation Spectra. IR. 3-Fluoro-3-(trifluoromethyl)diazirine (4). From a 1:3000 mixture of diazirine **4** in argon, 100 Torr was deposited. IR (argon matrix): 1589.5 (w), 1351.5 (vs), 1339.2 (w), 1231.5 (s), 1200.6 (vs), 1074.1 (vs), 771.2 (w), 599.8 (w), 570.1 (w) cm^{-1}.

3-Chloro-3-(trifluoromethyl)diazirine (5). From a 1:3000 mixture of diazirine **5** in argon, 100 Torr was deposited. IR (argon matrix): 1602.5 (w), 1300.0 (vs), 1212.4 (vs), 1198.0 (vs), 1190.7 (m), 1080.8 (w), 962.2 (s), 737.7 (w) cm^{-1}.

3-Bromo-3-(trifluoromethyl)diazirine (6). From a 1:3000 mixture of diazirine **6** in argon, 100 Torr was deposited. IR (argon matrix): 1598.4 (m), 1291.3 (vs), 1285.0 (s), 1208.3 (vs), 1196.3 (vs), 923.4 (vs), 725.7 (m), 570.0 (w) cm^{-1}.

Fluoro(trifluoromethyl)carbene (1). Photolysis of matrix-isolated diazirine **4** for 2 h ($\lambda = 316$ nm) led to complete disappearance of the diazirine bands and growth of bands assigned to carbene **6**. Several nonphotolabile bands which matched the positions and intensities of an authentic sample of bromotrifluoromethane were also observed. ^{19}F NMR showed this impurity to be present in the diazirine sample as an inseparable side product of the fluoride exchange reaction. IR of **1** (argon matrix): see Table I. IR of CF_3Br (argon matrix): 1201.3 (vs), 1199.4 (vs), 1197.4 (vs), 1075.7 (vs), 761.0 (w), 758.2 (w) cm^{-1}.

Chloro(trifluoromethyl)carbene (2). Photolysis of matrix-isolated **5** for 1 h ($\lambda = 318$ nm) led to the complete disappearance of the diazirine bands and growth of bands assigned to carbene **2**. A small amount of bands assigned to alkene **11** (<5%) was also observed which could be augmented with further irradiation. IR of **2** (argon matrix): see Table I.

Bromo(trifluoromethyl)carbene (3). Photolysis of matrix-isolated **6** for 1 h ($\lambda = 330$ nm) led to the complete disappearance of the diazirine bands and generation of bands assigned to carbene **3**. A small amount of bands assigned to alkene **12** (10%) was also observed which could be augmented with further irradiation. IR of **3** (argon matrix): see Table I.

Bromo(trifluoromethyl)diazomethane (13). From a 1:3000 mixture of diazirine **6** in nitrogen, 100 Torr was deposited. Photolysis of the matrix for 6 h ($\lambda = 340$ nm) led to complete disappearance of the diazirine bands and growth of bands assigned to carbene **3** (50%), alkene **12** (40%), and diazo compound **13** (10%). Continued photolysis for 6.5 h ($\lambda = 265$ nm) resulted in a loss of carbene band intensity (10%) while an increase was observed for the IR bands of alkene **12** (50%) and diazo compound **13** (40%). Irradiation for 45 min ($\lambda = 460$ nm) then led to a decrease in the diazo bands (5%) and an increase in the carbene **3** (25%) and alkene **12** (70%) intensities. Broad-band irradiation of the matrix for 6 h ($\lambda > 280$ nm) led to a complete loss of carbene and diazo IR bands, and only bands assigned to alkene **12** were observed. IR of **13** (N_2 matrix): 2094.6 (vs), 1350.1 (s), 1234.6 (m), 1170.2 (m), 1136.7 (s), 969.2 (s), 731.7 (w) cm^{-1}.

2-Chloro-1,1,1,2-tetrafluoroethane (7). A 120-Torr sample of a 1:4:1570 mixture of diazirine **4**, HCl, and argon was deposited at approximately 2 Torr/min at 23 K. Photolysis of the matrix for 1 h ($\lambda = 316$ nm) produced bands assigned to carbene **1** and small amounts of ethane **7** (5%) and a mixture of *cis*- and *trans*-perfluoro-2-butene (2%). Raising the window temperature to 38–39 K and maintaining that temperature for 7.5 h led to an approximate 80% reduction in the carbene band intensities. Concomitant growth of bands assigned to ethane **7** (70%) and butenes (30%) was observed. The wavenumber positions and intensities for ethane **7** matched those of an authentic sample matrix isolated in argon. *cis*- and *trans*-perfluoro-2-butene positions and intensities matched closely those reported in the literature.[13] IR of **7** (argon matrix): 3009.5 (vw), 1377.8 (m), 1297.1 (s), 1282.8 (vs), 1207.4 (vs), 1162.5 (vs), 1096.0 (vs), 884.5 (s), 816.8 (s), 695.8 (s) cm^{-1}. IR of *cis*-octafluoro-2-butene (argon matrix): 1733.6 (w), 1348.6 (m), 1243.5 (vs), 1225.2 (vs), 1194.8 (s), 1109.7 (m), 925.5 (m), 721.6 (w) cm^{-1}. IR of *trans*-octafluoro-2-butene (argon matrix): 1295.1 (m), 1240.4 (m), 1194.8 (s), 886.7, 684.7 (m) cm^{-1}.

2,2-Dichloro-1,1,1-trifluoroethane (8). A 110-Torr sample of a 1:4:1650 mixture of diazirine **5**, HCl, and argon was deposited at approximately 2 Torr/min at 23 K. Photolysis of the matrix at 23 K for 1 h ($\lambda = 318$ nm) produced bands assigned to carbene **2** and small amounts of alkene **11** (<2%) and ethane **8** (5%). Raising the window temperature to 38–39 K and maintaining that temperature for 8 h led to an approximate 90% reduction in the carbene band intensities. Concomitant growth of bands assigned to ethane **8** was observed which matched the wavenumber band positions and intensities of an authentic sample of matrix-isolated **8**. IR of **8** (argon matrix): 3026.6 (vw), 1323.6 (vs), 1277.1 (vs), 1189.5 (vs), 1143.0 (vs), 1068.3 (s), 873.2 (m), 837.5 (vs), 768.5 (m), 672.6 (s), 555.9 (vw), 527.7 (vw) cm^{-1}.

2-Bromo-2-chloro-1,1,1-trifluoroethane (9). A 105-Torr sample of a 1:4:1700 mixture of diazirine **6**, HCl, and argon was deposited at approximately 2 Torr/min at 23 K. Photolysis of the matrix at 23 K for 1 h ($\lambda = 330$ nm) produced bands assigned to carbene **3** and small amounts of bands assigned to alkene **12** (<5%) and ethane **9** (10%). Raising the window temperature to 38–39 K and maintaining that temperature for 8 h led to an approximate 70% reduction in the carbene band intensities. Concomitant growth of bands assigned to ethane **9** was observed which matched the wavenumber positions and intensities of an authentic sample of matrix-isolated **9**. IR of **9** (argon matrix): 3030.7 (vw), 1313.7 (vs), 1269.3 (vs), 1197.2 (s), 1182.3 (vs), 1131.0 (vs), 868.4 (w), 812.2 (vs), 716.8 (m), 664.7 (m) cm^{-1}.

Tetrafluoroethene (10). Broad-band photolysis of matrix-isolated carbene **1** (2.5 h, $\lambda > 280$; 0.7 h, $\lambda > 220$ nm; 0.3 h, $\lambda > 185$ nm) led to an approximate 60% reduction of the carbene bands and growth of bands assigned to alkene **10**. The band positions and intensities matched closely those reported in the literature.[30] IR of **10** (argon matrix): 1327.4 (vs), 1179.6 (vs) cm^{-1}.

Chlorotrifluoroethene (11). Broad-band photolysis of matrix-isolated carbene **2** (2 h, $\lambda = 280$–450 nm; 0.5 h, $\lambda > 280$ nm; 0.5 h, $\lambda > 220$ nm) led to an approximate 70% reduction of the carbene bands and growth of bands assigned to alkene **11**. The band positions and intensities matched those of an authentic sample[31] of matrix-isolated **11**. IR of **11** (argon matrix): 1798.0 (vs), 1330.8 (vs), 1219.6 (vs), 1205.4 (vs), 1074.5 (vs), 1054.3 (vs), 693.1 (w) cm^{-1}.

Bromotrifluoroethene (12). Broad-band photolysis of matrix-isolated carbene **3** (8 h, $\lambda = 280$–450 nm) led to a greater than 95% reduction

---

(30) Nielsen, J. R.; Claassen, H. H.; Smith, D. C. *J. Chem. Phys.* **1950**, *18*, 812.

(31) Mann, D. E.; Acquista, N.; Plyler, E. K. *J. Chem. Phys.* **1953**, *21*, 1949.

of the carbene bands and growth of bands assigned to alkene **12**. The band positions and intensities match closely those reported in the literature.[32] IR of **12** (argon matrix): 1784.8 (vs), 1321.9 (vs), 1221.6 (vs), 1199.6 (vs), 1071.4 (m), 1037.1 (s), 1020.0 (vs), 695.8 (w), 667.6 (w) cm^{-1}.

Matrix Isolation Spectra. UV. 3-Fluoro-3-(trifluoromethyl)diazirine (4). From a 1:480 mixture of diazirine **4** in argon, 130 Torr was deposited. UV (argon matrix): λ_{max} = 328, 313 nm. See also Results.

3-Chloro-3-(trifluoromethyl)diazirine (5). From a 1:250 mixture of diazirine **5** in argon, 180 Torr was deposited. UV (argon matrix): λ_{max} = 332, 318 nm. See also Results.

3-Bromo-3-(trifluoromethyl)diazirine (6). From a 1:200 mixture of diazirine **6** in argon, 190 Torr was deposited. UV (argon matrix): λ_{max} = 334, 320 nm. See also Results.

Fluoro(trifluoromethyl)carbene (1). Photolysis of matrix-isolated **4** at 12 K for 1.3 h (λ = 316 nm) resulted in complete loss of the diazirine absorptions and generation of two new absorptions assigned to carbene **1**. UV of **1** (argon matrix): λ_{max} = 465 ($\epsilon \approx$ 100 (L cm^{-1})/mol), 230 nm. See also Results.

Chloro(trifluoromethyl)carbene (2). Photolysis of matrix-isolated **5** at 12 K for 1.5 h (λ = 318 nm) resulted in complete loss of the diazirine absorptions and generation of two new absorptions assigned to carbene **2**. UV of **2** (argon matrix): λ_{max} = 640 ($\epsilon \approx$ 60 (L cm^{-1})/mol), 235 nm. See also Results.

Bromo(trifluoromethyl)carbene (3). Photolysis of matrix-isolated **6** at 12 K for 1.5 h (λ = 320 nm) resulted in complete loss in the diazirine absorptions and generation of two new absorptions assigned to carbene **3** in addition to a small band at 400 nm. Subsequent photolysis at 400 nm (15 min) completely destroyed the 400-nm absorption with no change in the remaining spectrum. UV of **3** (argon matrix): λ_{max} = 665 ($\epsilon \approx$ 45 (L cm^{-1})/mol), 270 (sh), 235 nm. See also Results.

Acknowledgment. We are grateful to the National Science Foundation (Grant CHE-8822674) for support of this work and to Dr. George Furst for help with the FTIR. The Research Foundation at the University of Pennsylvania generously provided funds to upgrade the departmental FTIR facility. W.P.D. thanks the Alfred P. Sloan Foundation for a research fellowship (1990–1992).

Registry No. 1, 58734-91-1; **2**, 22189-12-4; **3**, 139871-62-8; **4**, 117113-32-3; **5**, 58911-30-1; **6**, 117113-33-4; **7**, 2837-89-0; **8**, 306-83-2; **9**, 151-67-7; **10**, 116-14-3; **11**, 79-38-9; **12**, 598-73-2; **13**, 139871-63-9; **14**, 13453-52-6; **15**, 2108-20-5; **16**, 17141-28-5; HCl, 7047-01-0; N_2, 7727-37-9; trifluoroacetamidine, 354-37-0; (trifluoromethyl)diazomethane, 371-67-5; *tert*-butyl hypobromite, 1611-82-1; *cis*-perfluoro-2-butene, 1516-65-0; *trans*-perfluoro-2-butene, 1516-64-9.

---

(32) Mann, D. E.; Acquista, N.; Plyler, E. K. *J. Chem. Phys.* **1954**, *22*, 1199.

Triplet and Singlet Energy Transfer in Carotene–Porphyrin Dyads: Role of the Linkage Bonds

Devens Gust,* Thomas A. Moore,* Ana L. Moore,* Chelladurai Devadoss, Paul A. Liddell, Roel Hermant, Ronald A. Nieman, Lori J. Demanche, Janice M. DeGraziano, and Isabelle Gouni

Contribution from the Department of Chemistry and Biochemistry and Center for the Study of Early Events in Photosynthesis, Arizona State University, Tempe, Arizona 85287-1604.

Received October 17, 1991

Abstract: A series of carotenoporphyrin dyad molecules in which the carotenoid is covalently linked to a tetraarylporphyrin at the ortho, meta, or para position of a meso aromatic ring has been prepared, and the molecules have been studied using steady-state and transient fluorescence emission, transient absorption, and ^1H NMR methods. Triplet–triplet energy transfer from the porphyrin moiety to the carotenoid has been observed, as has singlet–singlet energy transfer from the carotenoid polyene to the porphyrin. In addition, the carotenoid quenches the fluorescence of the attached porphyrin by a mechanism which increases internal conversion. The rates of all three of these processes are slower for the meta isomer than for the corresponding ortho and para molecules. Analysis of the data suggests that the triplet–triplet energy transfer is mediated by a through-bond (superexchange) mechanism involving the π-electrons of the linkage bonds, rather than a direct, through-space coupling of the chromophores. The same appears to be true for the process leading to enhanced internal conversion. The results are consistent with a role for the through-bond mechanism in the singlet–singlet energy transfer as well. Simple Hückel molecular orbital calculations are in accord with the proposed through-bond process.

Photochemical interactions between carotenoid polyenes and closely associated cyclic tetrapyrroles are important aspects of photosynthesis. For example, carotenoids provide photoprotection by rapidly quenching chlorophyll triplet states which are formed in antenna systems or photosynthetic reaction centers. This triplet–triplet energy transfer prevents chlorophyll-sensitized production of singlet oxygen, which is injurious to the organism.[1-6] In addition, carotenoids act as antennas by absorbing light in spectral regions where chlorophyll absorbs weakly and delivering the resulting excitation to chlorophyll via a singlet–singlet energy-transfer process.[7-11] Finally, chlorophyll first excited singlet states are quenched by nearby carotenoids.[12-14] This quenching has been ascribed to energy transfer,[15] or to electron transfer[12]

---

(1) Griffiths, M.; Sistrom, W. R.; Cohen-Bazire, G.; Stanier, R. Y. *Nature* **1955**, *176*, 1211.

(2) Cohen-Bazire, G.; Stanier, R. Y. *Nature* **1958**, *181*, 250.

(3) Foote, C. S.; Denny, R. W. *J. Am. Chem. Soc.* **1968**, *90*, 6233.

(4) Foote, C. S.; Chang, Y. C.; Denny, R. W. *J. Am. Chem. Soc.* **1970**, *92*, 5216.

(5) Monger, T. G.; Cogdell, R. J.; Parson, W. W. *Biochim. Biophys. Acta* **1976**, *449*, 136.

(6) Davidson, E.; Cogdell, R. J. *Biochim. Biophys. Acta* **1981**, *635*, 295.

(7) Goedheer, J. D. *Biochim. Biophys. Acta* **1969**, *172*, 252.

(8) Bazzaz, M. B.; Govindjee *Plant Physiol.* **1973**, *52*, 257.

(9) Cogdell, R. J.; Hipkins, M. F.; MacDonald, W.; Truscott, T. G. *Biochim. Biophys. Acta* **1981**, *634*, 191.

(10) Cogdell, R. J.; Frank, H. A. *Biochim. Biophys. Acta* **1987**, *895*, 63.

(11) Sauer, K. *Acc. Chem. Res.* **1978**, *11*, 257.

(12) Beddard, G. S.; Davidson, R. S.; Trethewey, K. R. *Nature* **1977**, *267*, 373.

(13) Gust, D.; Moore, T. A.; Liddell, P. A.; Nemeth, G. A.; Makings, L. R.; Moore, A. L.; Barrett, D.; Pessiki, P. J.; Bensasson, R. V.; Rougée, M.; Chachaty, C.; De Schryver, F. C.; Van der Auweraer, M.; Holzwarth, A. R.; Connolly, J. S. *J. Am. Chem. Soc.* **1987**, *109*, 846.

(14) Moore, T. A.; Gust, D.; Hatlevig, S.; Moore, A. L.; Makings, L. R.; Pessiki, P. J.; De Schryver, F. C.; Van der Auweraer, M.; Lexa, D.; Bensasson, R. V.; Rougée, M. *Isr. J. Chem.* **1988**, *28*, 87.

0002-7863/92/1514-3590$03.00/0