Electronic Structure of Carbenes. I. CH_2, CHF, and CF_2[1]

James F. Harrison

*Contribution from the Department of Chemistry, Michigan State University,
East Lansing, Michigan 48823. Received November 4, 1970*

Abstract: *Ab initio* molecular wave functions have been constructed for the lowest doubly occupied singlet state of CH_2, FCH, and CF_2 as a function of angle using a gaussian-lobe basis and the Hartree–Fock–Roothaan technique. The theoretical angles 105, 104, 105° compare well with the experimental values of 102.4, 102, 105° for CH_2, FCH, and CF_2, respectively. Similarities in the charge distribution of these systems have been studied using contour maps of the electronic density supplemented by the Mulliken population analysis. The carbon 1s energy is found to be a linear function of the charge on the carbon atom. The Koopmans theorem ionization potential for CF_2 (13.34 eV) is too high by approximately 1.5 eV; this is interpreted in terms of the charge redistribution in the resulting positive ion, which is expected to be extensive in CF_2^+. The ionization potential of FCH is estimated as 10.75 eV. The electrophilic character in the series is correlated with the population of the carbon p_π orbital and leads to the expectation that the electrophilicity should decrease along the series $CH_2 >$ FCH $> CF_2$. After an analysis of the probable errors involved in using a minimal virtual orbital representation of the lowest triplet and first two excited singlets, we constructed small CI's for the four lowest states and obtained the energy variation with angle. In the following we enclose the experimental number and theoretical counterpart in parentheses, with the experimental result first: $CF_2\ ^1A_1$ (104.9, 105°) $< {}^3B_1$ (?, 120°) $< {}^1B_1$ (122.3, 122.5°), with $\tilde{A}^1B_1 \leftarrow \tilde{X}^1A_1$ (4.62, 4.62 eV) and $E(^3B_1) - E(^1A_1) = 39$ kcal; FCH $^1A'$ (101.6, 104°) $\simeq {}^3A''$ (?, 122°) $< {}^1A''$ (127.2, 128°), with $\tilde{A}^1A'' \leftarrow \tilde{X}^1A'$ (2.14, 2.14 eV) and, as indicated, $E(^3A'') - E(^1A') \simeq 0$; $CH_2\ ^3B_1$ ($\simeq$ 136, 132.5°) $< {}^1A_1$ (102.4, 105°) $< {}^1B_1$ ($\simeq$ 140, 180°), with $\tilde{A}^1B_1 \leftarrow \tilde{X}^1A_1$ (0.88, 0.64 eV) and $E(^3B_1) - E(^1A_1) = -24$ kcal. An analysis of the probable errors in the CH_2 potential energy curves causes us to lower the estimate of the singlet–triplet separation to 19 kcal.

Carbenes[2] (methylenes) are divalent carbon compounds of considerable importance in synthetic chemistry. While these reactive intermediates are often invoked[3] in the formulation of reaction mechanisms, little is known of their physical properties, *i.e.*, geometry, charge distribution, spin multiplicity, etc. The characteristic carbene reactivity which brings them to the fore in synthetic chemistry proves to be the bane of those who seek to determine these physical properties experimentally.[4]

Ab initio molecular electronic structure theory has developed to the point where one is able to treat fairly routinely, although with as yet ill-defined reliability, systems with up to 40 electrons.[5] While carbenes present characteristic problems for the theoretician they are of the same order of magnitude of difficulty as those involved in studying less reactive systems. It is our intent to study a number of carbenes at an *ab initio* level, paying particular attention to charge distribution (as reflected in the Mulliken population analysis and charge density contour maps), geometry, singlet–triplet separation, electrophilic and nucleophilic characteristics, and the electronic spectra associated with valence-state excitations.

The series CH_2, CHF, and CF_2 has been selected for this initial study because comparison with the relatively reliable experimental data[4,6,7] available for these molecules will allow us to evaluate the efficacy of the theoretical techniques which we use.

Lowest Doubly Occupied Singlet States

A. Basis Set. We employ the gaussian-lobe representation of the atomic Hartree–Fock orbitals as given by Whitten.[8] As used in this study the s orbitals of carbon (or fluorine) are represented by ten 1s gaussians contracted according to their range (*i.e.*, short → long) into four groups of four, three, two, and one components each, while the p orbitals are represented by ten 1s gaussians contracted into two groups of eight (short range) and two (long range) components, respectively. This means that for each heavy atom (C or F) in the calculation we have six coefficients to be determined by the SCF procedure. The hydrogen function employed was found by optimally scaling the five-component lobe-function representation of the hydrogen 1s function in the experimental equilibrium configuration for the lowest doubly occupied singlet and then splitting this into two groups of three (short range) and two (long range) gaussian s functions, respectively. Each hydrogen atom contributes two coefficients to those being determined by the SCF procedure.

B. SCF. An *ab initio* SCF–MO function was constructed for several angles for the lowest doubly occupied singlet state of the three carbenes using the Hartree–Fock–Roothaan[9] procedure. All CF_2 and

(1) Supported in part by a grant from Research Corporation.
(2) See footnote 9 in W. von E. Doering and L. H. Knox, *J. Amer. Chem. Soc.*, **78**, 4947 (1956), for the origin of the name carbene.
(3) See, for example, W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964.
(4) (a) G. Herzberg, *Proc. Roy. Soc., Ser. A*, **262**, 291 (1961); *Ser. A*, **295**, 107 (1966); (b) R. A. Bernheim, H. W. Bernard, P. S. Wang, L. S. Wood, and P. S. Shell, *J. Chem. Phys.*, **53**, 1280 (1970); (c) E. Wasserman, W A. Yager, and V. J. Kuck, *Chem. Phys. Lett.*, **7**, 409 (1970); E. Wasserman, V. J. Kuck, R. S. Hutton, and W. A. Yager, *J. Amer. Chem. Soc.*, **92**, 7491 (1970); (d) G. Herzberg and J. W. C. Johns, *J. Chem. Phys.*, **54**, 2276 (1971).
(5) Examples from the recent literature include (a) S. D. Peyerimhoff and R. J. Buenker, *ibid.*, **51**, 2528 (1969), allylic systems; (b) J. R. Lombardi, W. Klemperer, M. B. Robin, H. Basch, and N. A. Kuebler, *ibid.*, **51**, 33 (1969), difluorodiazirine.

(6) (a) A. J. Merer and D. N. Travis, *Can. J. Phys.*, **44**, 1541 (1966), FCH structure and spectroscopy; (b) F. X. Powell and D. R. Lide, Jr., *J. Chem. Phys.*, **45**, 1067 (1966), CF_2 structure and dipole moment.
(7) C. W. Mathews, *Can. J. Phys.*, **45**, 2355 (1967), CF_2 structure and spectroscopy.
(8) J. L. Whitten, *J. Chem. Phys.*, **44**, 359 (1966).
(9) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

Table I. Energy (au) of CF_2 ($E = -236.0 - \epsilon$) in Various States

θ, deg ϵ	SCF [$\psi(\sigma^2)$]	¹A₁		¹A₁*		³B₁		¹B₁	
		ψ_-	CI	ψ_+	CI	$\psi(\sigma p)$	CI	$\psi(\sigma p)$	CI
100.0	0.6051	0.6118		0.1864		0.5045		0.3990	
104.9	0.6074	0.6143	0.6161	0.2049	0.2437	0.5153	0.5413	0.4104	0.4305
110.0	0.6052	0.6123		0.2206		0.5226		0.4183	
120.0	0.5901	0.5977	0.5998	0.2443	0.2843	0.5278	0.5536	0.4252	0.4460
125.0	0.5780	0.5859		0.2532		0.5269		0.4252	
130.0	0.5633	0.5716		0.2607		0.5238		0.4232	
134.8	0.5468	0.5557	0.5586	0.2667	0.3123	0.5191	0.5451	0.4197	0.4415

Table II. Energy (au) of FCH ($E = -137.0 - \epsilon$)

θ, deg ϵ	SCF [$\psi(\sigma^2)$]	¹A′		¹A′*		³A′′		¹A′′	
		ψ_-	CI	ψ_+	CI	$\psi(\sigma p)$	CI	$\psi(\sigma p)$	CI
100.0	0.7238	0.7285	0.7312	0.4494	0.4990	0.6833	0.7138	0.6119	0.6315
103.0	0.7245	0.7293		0.4566		0.6879		0.6164	
105.0	0.7244	0.7293	0.7322	0.4612	0.5114	0.6906	0.7213	0.6191	0.6389
107.5	0.7238	0.7287		0.4667		0.6934		0.6221	
110.0	0.7226	0.7276		0.4720		0.6957		0.6247	
120.0	0.7123	0.7176	0.7213	0.4904	0.5420	0.7004	0.7318	0.6313	0.6519
123.5	0.7069	0.7124		0.4959		0.7005		0.6322	
127.2	0.7003	0.7060	0.7101	0.5012	0.5535	0.6997	0.7315	0.6326	0.6537
130.5	0.6938	0.6996		0.5055		0.6983		0.6323	
132.8	0.6890	0.6948		0.5083		0.6969		0.6318	
135.0	0.6841		0.6950		0.5638		0.7278		0.6530

HCF calculations were carried out using the experimental[6,7] internuclear distances appropriate for the lowest singlet, while for CH_2 we used the singlet bond length in the range $100° \leq \theta \leq 120°$ and that appropriate for the triplet in the range $120° \leq \theta \leq 180°$. The molecular energies are presented in column 2 of Tables I, II, and III, the coordinate systems employed are displayed in Figure 1, and the angular dependence of the energy is shown in Figure 2. We have collected some relevant experimental data in Table IV, and a comparison of the tabulated bond angles with those in Figure 2 indicates satisfactory agreement.
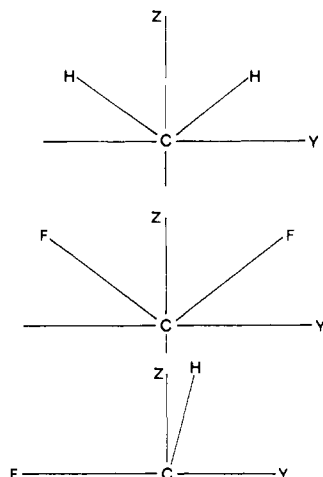

Figure 1. Coordinate systems.

Previous theoretical studies of CH_2 have been reviewed recently[10,11] and need not be considered here. Suffice it to say that the CH_2 SCF function which we

(10) J. F. Harrison in "Carbene Chemistry," W. Kirmse, Ed., Academic Press, New York, N. Y., in press.

(11) J. F. Harrison and L. C. Allen, *J. Amer. Chem. Soc.*, **91**, 807 (1969).

have constructed is not the best (energetically) available but is of a quality comparable to the HCF and CF_2 functions reported in this work. Since we are interested in characterizing trends in this sequence of carbenes,
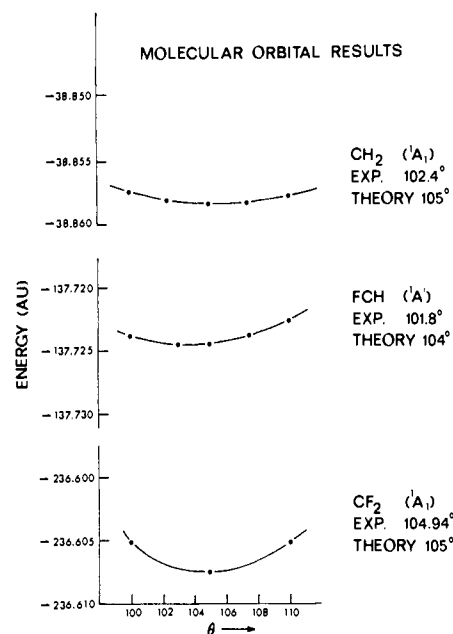

Figure 2. Energy *vs.* angle (MO-SCF representation of lowest double occupied singlet).

having all molecules represented at approximately the same level is desirable. Recently Sachs, Geller, and Kaufman[12] published the first *ab initio* representation of the lowest ¹A₁ state of CF_2. They used several nuclear-centered gaussian basis sets, the most extensive being a 9s5p basis which at the experimental[6,7] geometry

(12) L. M. Sachs, M. Geller, and J. J. Kaufman, *J. Chem. Phys.*, **51**, 2771 (1969).

Harrison | Electronic Structure of Carbenes

Table III. Energy (au) of CH₂ ($E = -38.0 - \epsilon$)

θ, deg	ε SCF [ψ(σ²)]	¹A₁ ψ₋	¹A₁ CI	¹A₁* ψ₊	¹A₁* CI	³B₁ ψ(σp)	³B₁ CI	¹B₁ ψ(σp)	¹B₁ CI
100.0	0.8574	0.8631	0.8679	0.6321	0.6907	0.8525	0.8872	0.7811	0.8041
105.0	0.8583	0.8640	0.8690	0.6466	0.7051	0.8589	0.8936	0.7896	0.8127
110.0	0.8578	0.8635	0.8687	0.6599	0.7182	0.8640	0.8986	0.7967	0.8200
125.0	0.8477	0.8539	0.8606	0.6904	0.7494	0.8717	0.9070	0.8095	0.8335
130.0	0.8440	0.8502	0.8576	0.7001	0.7585	0.8725	0.9079	0.8125	0.8369
135.0	0.8397	0.8461	0.8544	0.7089	0.7664	0.8724	0.9080	0.8146	0.8395
140.0	0.8352	0.8418	0.8512	0.7168	0.7732	0.8716	0.9073	0.8159	0.8415
150.0	0.8262	0.8332	0.8457	0.7300	0.7834	0.8685	0.9044	0.8167	0.8438
160.0	0.8185	0.8260	0.8427	0.7395	0.7889	0.8646	0.9005	0.8162	0.8449
180.0							0.8956		0.8454

Table IV. Experimental Data

	CF₂	FCH	CH₂
Geometry (bond length, Å, angle, deg)	¹A₁ (1.300, 104.94)ᵃ ³B₁ (?) ¹B₁ (1.32, 122.3)ᵈ	¹A′ (R_{CH} = 1.12, R_{CF} = 1.31, 101.8)ᵇ ³A″ (?) ¹A″ (R_{CH} = 1.12, R_{CF} = 1.29, 127.2)ᵇ	¹A₁ (1.11, 102.4)ᶜ ³B₁ (1.08, ≃136)ᶜ ¹B₁ (1.05, ≃140)ᶜ
Singlet–singlet transition, eV	Ã¹B₁ ← X̃¹A₁, 4.62ᵈ	Ã¹A″ ← X̃¹A′, 2.14ᵇ	B̃¹B₁ ← Ã¹A₁, 0.88ᶜ
Ground-state multiplicity	Singletᵉ	Singletᵇ	Tripletᶜ

ᵃ References 6b and 7. ᵇ Reference 6a. ᶜ Reference 4. ᵈ Reference 7. ᵉ Reference 6b.

($\theta = 104.8°$, $R = 1.300$ Å) resulted in a total energy of −236.64937 au, which is 0.04193 au lower than our SCF result. Less extensive basis sets were used to study the angle dependence of the energy and a 5s2p

distribution in HCF is very similar to that in HOF which was discussed in detail by Buenker,[13] *et al.*

In Figure 3 we consider those aspects of the charge distribution common to all three systems and we
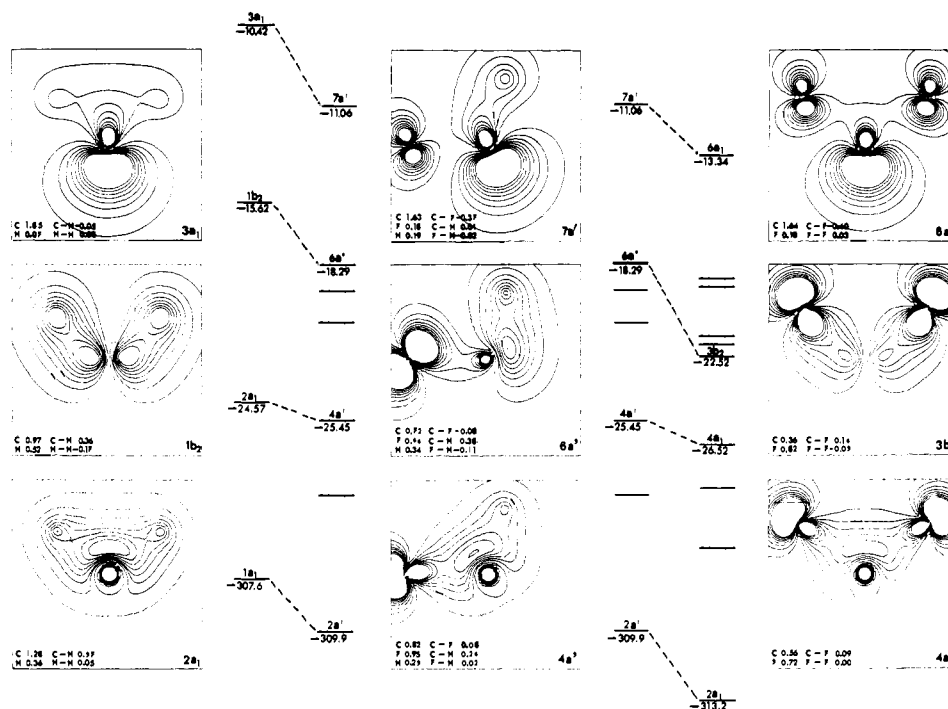

Figure 3. Correlation of the MO's of CF₂, FCH, and CH₂ at 105°.

basis predicts an equilibrium angle of 105.8° ($E = $ −234.8750 au) with the experimental bond length.

There have been no published *ab initio* studies of the electronic structure of HCF.

C. Charge Distribution. The detailed bonding–antibonding characteristics of CF₂ have been discussed by Sachs,[12] *et al.*, and those of CH₂ by Harrison,[10] and they need not be repeated here. In addition, the charge

correlate the orbitals of CH₂ and the fluorinated carbenes as we replace one and then both hydrogens by fluorine. On each map we indicate how the Mulliken population analysis[14] (gross and overlap populations) partitions the charge. Note that the highest occupied MO in each carbene is localized essentially on carbon

(13) R. J. Buenker and S. D. Peyerimhoff, *J. Chem. Phys.*, **45**, 3682 (1966).
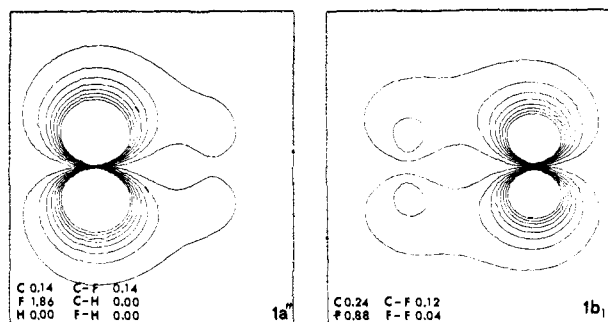(14) R. S. Mulliken, *ibid.*, **23**, 1833 (1955).

Figure 4. π system of CF_2 and CHF at 105°

Figure 5. Approximate energy required to remove a carbon 1s electron vs. charge (6 minus Mulliken gross population) on carbon.

and is readily interpreted as a lone-pair orbital. The polarity of the orbitals in the sequences $1b_2$, $6a'$, $3b_2$ (all ligand–ligand antibonding) and $2a_1$, $4a'$, $4a_1$ (all ligand–ligand bonding) changes dramatically as we substitute fluorine for hydrogen and reflects, of course, the large electronegativity of fluorine. Densities for the last sequence $1a_1$, $2a'$, $2a_1$ are not shown since they are localized entirely on carbon.

In Figure 4 we compare the charge distribution in the π system of CF_2 (the $1b_1$ orbital) and HCF (the $1a''$ orbital). Although the extent of π bonding is small, it is not negligible, and it seems to be more extensive in CF_2. We will return to this point later.

D. Carbon 1s Shifts. The lowest MO's correspond to highly localized densities easily associated with the 1s atomic orbital of either carbon or fluorine, and while the density of charge in these MO's remains localized and therefore atomic like, the energy required to remove an electron changes with bond angle, bond length, and the nature of the chemical environment. For example, from Figure 3 we note a substantial change in the carbon 1s energy as we substitute F for H in going from CH_2 to CF_2.

The advent of ESCA[15] has permitted inner-shell binding energies to be measured for a variety of systems with a resolution of 1 ppt. One of the most intriguing correlations to develop is the approximate linear relationship between these binding energies and the total charge on the atom host to the inner shell.[15-18] In Figure 5 we plot the one-electron energy associated with the carbon 1s MO vs. the charge on the carbon atom (charge being defined as atomic number minus carbon gross electron population[14]) for the carbenes CH_2, CHF, and CF_2, and in addition we plot the corresponding information for the fluorinated methanes.[19] Most strikingly, both sets of data yield straight lines which are parallel. This similarity in the slopes of both lines becomes more intriguing when we consider that (1) the C–H and C–F bond lengths differ for the two sets of compounds, (2) different quality atomic bases were used to represent the MO's in both studies, and (3) we are comparing a saturated carbon atom with an electron-deficient carbon atom.

(15) K. Siegbahn, et al., "ESCA Atomic Molecular and Solid State Structure Studied by Means of Electron Spectroscopy," Almqvist and Wiksells, Stockholm, Sweden, 1967.
(16) R. G. Albridge, U. Erickson, J. Hedman, C. Nordling, K. Siegbahn, and B. J. Lindberg, Ark. Kemi, 28, 257 (1968).
(17) J. M. Hollandef, D. N. Hendrickson, and W. L. Jolly, J. Chem. Phys., 49, 3315 (1968).
(18) H. Basch and L. C. Snyder, Chem. Phys. Lett., 3, 333 (1969).
(19) M. E. Schwartz, C. A. Coulson, and L. C. Allen, J. Amer. Chem. Soc., 92, 447 (1970).

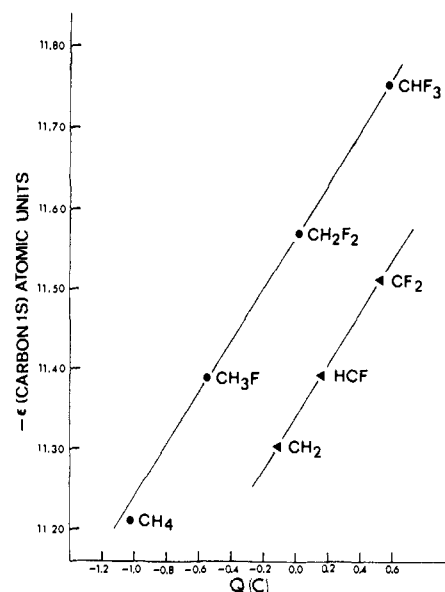In a recent study, Basch and Snyder[18] considered the variation of the K shell binding energies of C, N, O, F in various chemical environments. They found a linear relation between carbon 1s binding energy and net charge with a slope of 7.2 eV/excess electron, producing a best fit for 21 compounds. The slope of the plots in Figure 11 is 8.9 eV/excess electron, in good agreement with the Basch and Snyder study.

E. Ionization Potentials. Whether or not CF_2 has a larger ionization potential than CH_2 seems to depend on two opposing effects.[20] The most easily removed electron is essentially a carbon lone-pair electron, and the extent to which it is delocalized will depend on the electronegativity of the substituents. Increasing the electronegativity of the substituent will contribute to an increase in the ionization potential. The other effect is associated with the resulting positive ion. If the substituent can donate electrons to the electron-deficient (positive) carbon atom, one imagines the ion being stabilized by this ionic "resonance energy." This effect, i.e., electronic relaxation of the excited state, will tend to decrease the ionization potential.

In an MO–SCF theory the ionization potential of a particular electron is taken as the negative of the one-electron energy associated with the orbital hosting the electron. The efficiency of this association (Koopmans theorem[21]) is predicted on the assumption that the resulting positive ion is adequately described (at least in the ground-state geometry) by the neutral-molecule MO's, i.e., the electronic relaxation of the resulting positive ion is assumed to be negligible. In Figure 6 we plot the Koopmans theorem ionization potential against angle. The theoretical result for the $^1A_1$ state of CH_2 (10.4 eV) is not directly comparable to the experimental[22] result (10.39 eV), which is obtained from the Rydberg-series limit originating with the ground $^3B_1$ state. We may, however, estimate the ionization potential of the $^3B_1$ state as follows. The ionization of $^3B_1$ CH_2 will probably result in $^2A_1$ CH_2^+ (removal of a $1b_1$

(20) I. P. Fisher, J. N. Homer, and F. P. Lossing, ibid., 87, 957 (1965).
(21) T. A. Koopmans, Physica, 1, 104 (1933).
(22) G. Herzberg, Can. J. Phys., 39, 1511 (1961).

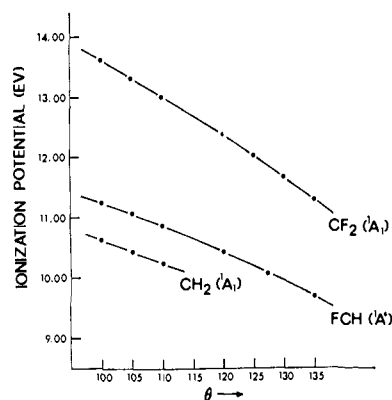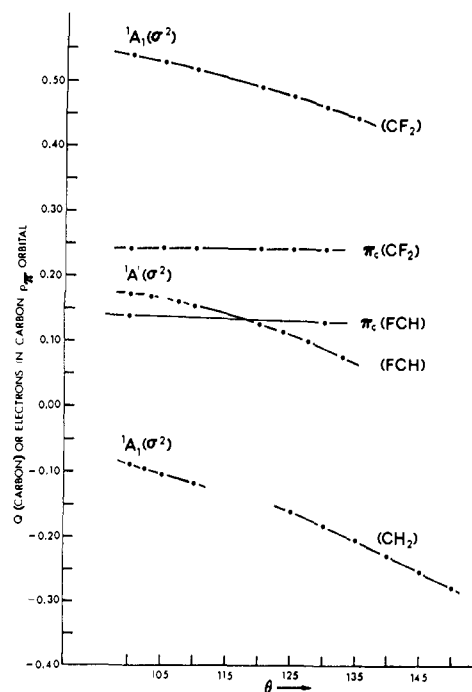Figure 6. Koopmans theorem ionization potential vs. angle for CF_2, FCH, and CH_2.

Figure 7. Charge (6 minus Mulliken gross population) on carbon vs. angle and number of electrons in the carbon p_π orbital vs. angle.

electron), which, because the $1b_1$ electron is essentially nonbonding, should have an energy vs. angle curve which is quite comparable in shape to that of $^3B_1$ CH_2. The Koopmans theorem ionization potential in $^1A_1$ CH_2 corresponds to a vertical excitation to CH_2^+ with an angle of approximately 105° and is larger than the energy separation between the minimum in the $^1A_1$ CH_2 and $^2A_1$ CH_2^+ curves by about as much as the difference $E(^3B_1, 105°) - E(^3B_1, 132°)$ or 9 kcal. Using our estimate of 19 kcal as the singlet–triplet separation in CH_2, we estimate that the $^2A_1$ state of CH_2^+ is 10.4 eV + 10 kcal or 10.8 eV above the $^3B_1$ state of CH_2. This is most likely an upper limit, since any reduction of the CH_2 singlet–triplet separation from 19 kcal will lower this estimate.

The CF_2 results (theory, 13.34; experimental,[23] 11.86 eV) both refer to the singlet state, and we are too high by 1.48 eV. There are no experimental data for HCF. If we assume that the Koopmans ionization potential faithfully reflects the electronegativity effect, then we may estimate that the electronic relaxation in CH_2^+ is small while that in CF_2^+ is sufficient to stabilize the ion by 1.5 eV, i.e., by approximately half of the increase due to the electronegativity charge. If we assume that the same ratios prevail in HCF we may estimate its ionization potential at 10.75 eV.

F. Relative Electrophilicity. Although difficult to prove, it is intuitively appealing to imagine a carbene attacking an olefinic double bond with its almost empty carbon P_π orbital, i.e., so that the initial transfer of charge from the olefin to the carbene is via this orbital.[24] If so, then we would expect the ease with which a member of a series of carbenes attacks a given olefin to be correlated with the number of electrons in the carbene carbon p_π orbital. In Figure 7 we plot this number for CF_2 and CHF along with the total charge (Mulliken gross population) on the carbene carbon as a function of angle. The p_π orbital is empty in CH_2 (at the SCF level). As expected, the carbon becomes more positive as the number of fluorines increases, but the loss of electrons is via the σ system since the C_{p_π} orbital gains electrons. Accordingly, we expect the electrophilicity to decrease along the series $CH_2 > CHF > CF_2$, even though the charge on the carbene carbon is becoming more positive. Furthermore, since the elec-

tronegativity of the halogens decreases as we go from F to I, we would expect less charge transfer in the σ system and consequently less transfer from halogen to carbon via the π system as we go from CF_2 to CI_2. We would then expect the occupancy of the carbon p orbital to decrease in the sequence CF_2, CCl_2, CBr_2, CI_2, CH_2, and would anticipate a decrease in the electrophilic character as we proceed from CH_2 to CF_2 in this series. This order was first predicted by Simons[25] and there is some evidence that it is the experimental order.[26]

Relative Energies of Singlets and Triplets

A. Virtual Orbital Approximation. The highest occupied MO in the sequence of carbenes under consideration is essentially a carbon lone pair orbital, while the lowest empty orbital is predominately carbon p_π. Following Hoffmann[27] we refer to these as σ and p, respectively. Designating those spatial orbitals below σ as the "core," we may construct the following representations for the first few low-lying states.

$$\psi(\sigma^2) = (\text{core } \sigma | \text{core } \sigma) \tag{1}$$

$$\psi(p^2) = (\text{core } p | \text{core } p) \tag{2}$$

$$^3\psi(\sigma p) = 2^{-1/2}[(\text{core } \sigma | \text{core } p) + (\text{core } p | \text{core } \sigma)] \tag{3}$$

$$^1\psi(\sigma p) = 2^{-1/2}[(\text{core } \sigma | \text{core } p) - (\text{core } p | \text{core } \sigma)] \tag{4}$$

where the symbol (|) represents a normalized Slater determinant and all spatial orbitals bearing α spins are to the left of the vertical bar while those with β spin are to the right.

(23) R. F. Pottie, J. Chem. Phys., 42, 2607 (1965).
(24) R. Hoffmann, R. Gleiter, and F. B. Mallory, J. Amer. Chem. Soc., 92, 1460 (1970).

(25) J. P. Simons, J. Chem. Soc., 5406 (1965).
(26) P. S. Skell and M. S. Cholod, J. Amer. Chem. Soc., 91, 7131 (1969).
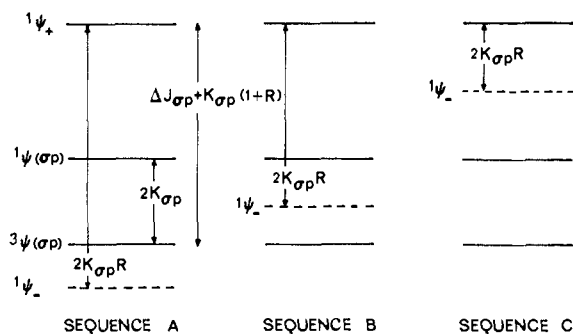(27) R. Hoffmann, G. D. Zeiss, and G. W. Van Dine, ibid., 90, 1485 (1968).

Figure 8. Possible state sequences for a carbene in virtual orbital approximation.

Since $\psi(\sigma^2)$ and $\psi(p^2)$ have the same symmetry, they will combine in a configuration interaction calculation to form the states

$$\psi_- = -\psi(\sigma^2) \sin \chi + \psi(p^2) \cos \chi \qquad (5)$$

$$\psi_+ = \psi(\sigma^2) \cos \chi + \psi(p^2) \sin \chi \qquad (6)$$

where χ is determined by the variation principle.
We define

$$E(\sigma^2) = \langle \psi(\sigma^2) | \hat{H} | \psi(\sigma^2) \rangle$$

$$E(p^2) = \langle \psi(p^2) | \hat{H} | \psi(p^2) \rangle$$

$$K_{\sigma p} = \int \sigma(1)p(1)r_{12}^{-1}\sigma(2)p(2)dV(1, 2) \qquad (7)$$

$$J_{\sigma\sigma} = \int \sigma(1)\sigma(1)r_{12}^{-1}\sigma(2)\sigma(2)dV(1, 2)$$

$$J_{\sigma p} = \int \sigma(1)\sigma(1)r_{12}^{-1}p(2)p(2)dV(1, 2)$$

where $\hat{H}$ is the exact Schrödinger Hamiltonian. The energies of the various states are given by

$$E_{\pm} = [E(\sigma^2) + E(p^2)]/2 \pm K_{\sigma p}R \qquad (8)$$

with

$$R = (\{[E(\sigma^2) - E(p^2)]/2K_{\sigma p}\}^2 + 1)^{1/2} \qquad (9)$$

also

$$^3E(\sigma p) = [E(\sigma^2) + E(p^2)]/2 -$$
$$(J_{\sigma\sigma} + J_{pp})/2 + J_{\sigma p} - K_{\sigma p} \qquad (10)$$

$$^1E(\sigma p) = {}^3E(\sigma p) + 2K_{\sigma p} \qquad (11)$$

Using the inequality derived by Roothaan[9]

$$0 \leq K_{\sigma p} \leq J_{\sigma p} \leq (J_{\sigma\sigma} + J_{pp})/2 \qquad (12)$$

we find

$$^3E(\sigma_p) < E_+$$
$$^1E(\sigma p) < E_+ \qquad (13)$$
$$^3E(\sigma p) < {}^1E(\sigma p)$$
$$E_- < E_+$$

Interestingly, within the virtual orbital approximation the relative position of three of the electronic states ψ_+, $^1\psi(\sigma p)$, and $^3\psi(\sigma p)$ is fixed but ψ_- is constrained only to lie below ψ_+. There are, then, within this theory, three possible excited-state sequences for the carbenes under consideration and these are shown in Figure 8. Note that in this figure

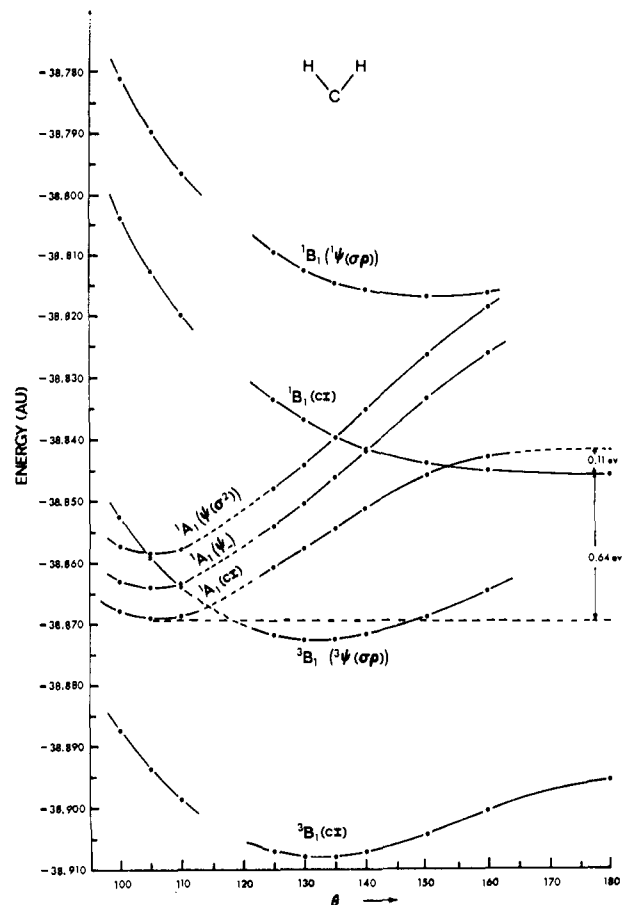$$\Delta J_{\sigma p} = (J_{\sigma\sigma} + J_{pp})/2 - J_{\sigma p} > 0$$

Figure 9. Total energy vs. bond angle for CH_2.

Arguments may be constructed which indicate that sequence C is very unlikely, and so we anticipate that the carbenes in question will follow either sequence A (singlet ground state) or sequence B (triplet ground state). Detailed considerations[10] indicate that the particular sequence obtained varies with internuclear angle, sequence B (triplet) obtaining in the linear configuration and at large angles and sequence A at smaller angles.

The energies of these states are among those shown as a function of bond angle in Figures 9–11.

From Table IV we see there are several quantities which we may compare with experiment to see how well we are doing, i.e., the spin multiplicity of the ground state, the bond angle in various states, and the energy of the 0–0 band in the lowest singlet–singlet transition.

Although in all three molecules the experimental evidence[4,6,7] for the ground-state multiplicity is rather indirect, it is satisfying that within the virtual orbital approximation we agree with the consensus of opinion that CHF and CF_2 are ground-state singlets while CH_2 is a triplet. With the possible exception of CH_2 the bond angle and lowest singlet–singlet transition energy are more firmly established than the ground-state multiplicity. As seen from Figures 9, 10, and 11 the bond angles are still in reasonable agreement with experiment but the transition energies (5.14, 2.64, and 1.29 eV for CF_2, FCH, and CH_2, respectively) are too high. The bond angle of triplet CH_2 (132.5°) is comparable to that predicted by every ab initio calculation to date,[11,28–30]

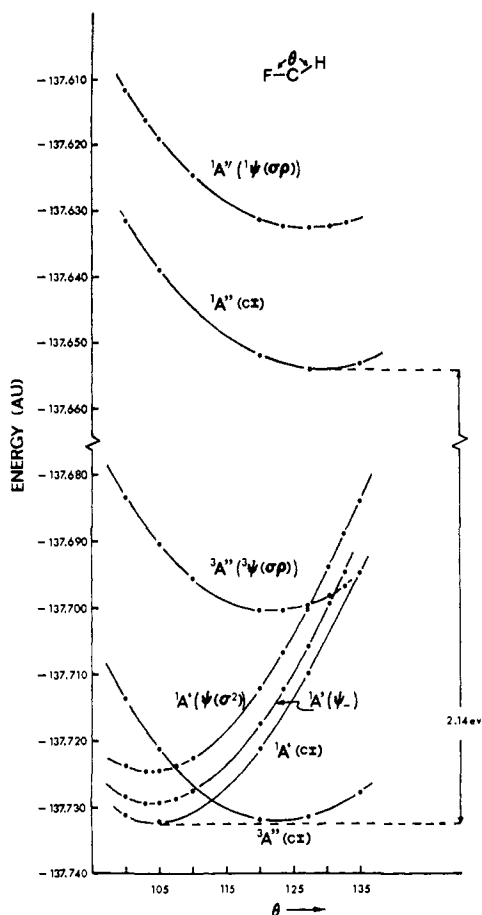(28) J. M. Foster and S. F. Boys, Rev. Mod. Phys., 26, 716 (1957).

Figure 10. Total energy *vs.* bond angle for FCH.

Figure 11. Total energy *vs.* bond angle for CF₂.

and although these differ significantly from the earlier experimental[4a] (linear) result they are in substantial agreement with the results of recent esr work[4b,c] and a reinterpretation of the earlier uv studies.[4d]
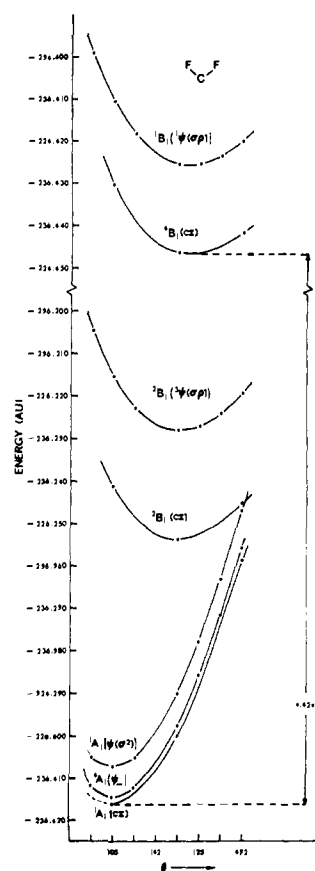
B. Sources of Error in the Preceding Theory. The preceding theory may be criticized on two counts. First, we anticipate that the first virtual orbital is a poor representation (too diffuse) of the *in situ* p orbital appropriate for the states arising from the σp and p^2 configurations. Secondly, there is a substantial difference in the correlation energy[31] associated with the σ^2 and σp configurations. We will assume that this correlation energy difference comes about primarily because of the dissolution of the σ ²lone pair. Insofar as the $\sigma^2 \rightarrow \sigma$p transition energies are concerned, it is the difference between the virtual orbital effect (operative in the excited state) and the correlation energy difference (associated with the ground state) which is of significance.

C. Improvement in the Representations of the Various States. If we were to carry out an SCF calculation for the $^3\psi(\sigma$p) and $^1\psi(\sigma$p) states we expect the form of the orbitals to change relative to the closed-shell set, but not the symmetry. Assuming that the orbitals which change most drastically from the closed-shell SCF are the σ and p we may approximate the open-

(29) C. F. Bender and H. F. Schaefer III, *J. Amer. Chem. Soc.*, **92**, 4984 (1970).
(30) W. Meyer, Arbeitsbericht Der Gruppe Quantenchemie, Max-Planck Institut für Physik und Astrophysik, No. 10, 1968.
(31) R. Lefebvre and C. Moser, Ed., "Correlation Effects in Atoms and Molecules," Interscience, New York, N. Y., 1969.

shell (σp) SCF solution by

$$^3\psi \sim [\text{core } (\sigma + \lambda\sigma')|\text{core } (p + \gamma p')] +$$
$$[\text{core } (p + \gamma p')|\text{core } (\sigma + \lambda\sigma')] \sim$$
$$^3\psi(\sigma p) + \lambda^3\psi(\sigma' p) + \gamma^3\psi(\sigma p') + \lambda\gamma^3\psi(\sigma' p') \quad (14)$$

where σ' and p' are additional virtual orbitals of the closed-shell problem and λ and γ are variation parameters. We of course have a comparable expression for the $^1\psi$ state. With this motivation we constructed a small configuration-interaction representation for the open-shell states of CF₂ using the four configurations shown in eq 14. For CH₂ and FCH these configurations were augmented by σ''p and σ''p', where σ'' is the second virtual orbital of σ symmetry. From Table I we see that the triplet is lowered more than the singlet and both lowerings are almost independent of bond angle. These states are labeled CI in Figures 9–11.

Now according to our analysis of the sources of error the energy difference between the SCF $\psi(\sigma^2)$ and this minimal CI representation of the $^1\psi$ and $^3\psi$ states should be smaller than the experimental value by a number which is approximately the correlation energy associated with the σ^2 lone pair. Since the $^1\psi_-$ state accounts for some of this correlation energy it is more appropriate to use $E(^1\psi_-)$ rather than $E(\sigma^2)$ in computing transition energies. With the exception of the CH₂ result the *ab initio* estimates of ν_{00} computed in this way (4.58, 2.05, and 0.50 eV for CF₂, FCH, and CH₂, respectively) compare well with the experimental values. If we further improve the representation of the lowest singlet state of CF₂ by performing a CI over the configurations σ^2, $\sigma\sigma'$, p^2, and pp', with CH₂ and HCF

being augmented by $\sigma\sigma''$ and $(p')^2$, we obtain the transition energies 4.62, 2.14, and 0.64 eV for CF_2, FCH, and CH_2 and the results labeled CI in Figures 9–11 and Tables I–III. While we are encouraged by the agreement with experiment, we consider it somewhat fortuitous since it is quite likely that the correlation energy loss upon dissolution of the σ^2 lone pair is greater[32] than the 0.25 eV we find from the minimal CI.

D. Singlet–Triplet Transition. In going from the $^3B_1$ state of CF_2 or CH_2 to the corresponding $^1B_1$ state we neither disrupt any existing nor form any new electron pairs and we therefore expect the correlation energy in these two states to be comparable. Consequently, we anticipate that the energy difference $^1B_1 - {}^3B_1$ or $^1A'' - {}^3A''$ should be adequately represented by the various CI functions we have described. To the extent that this is true we note that the reliability of our $^1A_1-{}^3B_1$ or $^1A'-{}^3A''$ separations may be estimated by observing how well we account for the various singlet–singlet transitions. Since we do very well in estimating this transition in CF_2 ($^1B_1 \leftarrow {}^1A_1$) and FCH ($^1A'' \leftarrow {}^1A'$) (see Table IV), we expect the singlet–triplet separations to be accurate, so in CF_2 we predict that the $^3B_1$ is 39 kcal above the $^1A_1$ state, while in FCH the $^1A'$ and $^3A''$ are separated by a very small ($\simeq 0$ kcal) energy. Also, since our computed energy for the

(32) Indeed E. A. Scarzafava, Ph.D. Thesis, Indiana University, 1969, estimates the correlation energy in an oxygen lone pair in the water molecule as approximately 1 eV.

$\bar{A}\,{}^1B_1 \leftarrow \bar{X}\,{}^1A_1$ transition in CH_2 is too low by 5 kcal we expect the $^3B_1$ to be 19 kcal below the $^1A_1$ state even though our raw data predict this separation to be 24 kcal.

Our estimate is in disagreement with recent experimental results[33] which indicate a separation of 1–2 kcal, and on the basis of the above arguments this would imply an error of 18 kcal in the $^1B_1-{}^3B_1$ separation, which seems unreasonable. However, since this discrepancy must be resolved, we are undertaking a detailed study of the correlation energy contribution to the various states of CH_2 and will report the results as soon as possible.[34]

Acknowledgment. The contour plots were constructed with routines written by Dr. Vincent Nicely, and it is a pleasure to acknowledge their use.

(33) R. W. Carr, Jr., T. W. Eder, and M. G. Topor, *J. Chem. Phys.*, **53**, 4716 (1970).

(34) NOTE ADDED IN PROOF. Recently, O'Neil, Schaefer, and Bender, manuscript in preparation, have used the iterative natural orbital technique [C. F. Bender and E. R. Davidson, *J. Phys. Chem.*, **70**, 2675 (1966)] to construct wave functions for various states of CH_2. Using Huzinaga's (9s5p/4s) basis [(S. Huzinaga, *J. Chem. Phys.*, **42**, 1293 (1965)] contracted to [4s2p/2s] as recommended by Dunning [T. H. Dunning, Jr., *J. Chem. Phys.*, **53**, 2823 (1970)], a 298 and a 408 configuration representation of the $^1A_1$ and $^3B_1$ states, respectively, were constructed as a function of geometry. Their result for the $^3B_1-{}^1A_1$ splitting, $E[^3B_1\,(133.3°)] - E[^1A_1\,(104.4°)] = -0.96$ eV (-22 kcal), is in substantial agreement with ours but is still in conflict with the interpretation of the experimental data of ref 33. I thank Professor Schaefer for forwarding the results of his study before publication.

Viscosity Dependence of Fluorescence Quantum Yields

S. Sharafy and K. A. Muszkat*[1]

*Contribution from the Department of Chemistry,
the Weizmann Institute of Science, Rehovot, Israel,
and the Physikalisch-Chemisches Institut der Universität Basel,
Basel, Switzerland. Received October 28, 1970*

Abstract: The normally nonfluorescent *cis*-stilbene and sterically hindered *trans*-stilbenes become strongly fluorescent in very viscous media. Thus a maximum fluorescence quantum yield (ϕ_F) of 0.75 is measured for *cis*-stilbene in a hydrocarbon glass. The fluorescence of these compounds is a steep function of the viscosity, due to a solvent free volume (and viscosity) dependent rate constant for the internal conversion ($S_1 \rightarrow S_0$) process. This dependence is traced to the effect of enhanced solvent viscosity in reducing the probability and amplitude of the twisting and out-of-plane-bending modes about the central double bond. The theoretical dependence of ϕ_F on viscosity is developed along the lines of the free volume theory of viscosity and is obeyed accurately by the experimental results. An uncoupling of fluorescence and intersystem crossing at high viscosities is observed for *trans-p*-bromostilbene and for *trans*-hexamethylstilbene. The photochemical significance of this uncoupling is examined.

The quantum yields of the trans to cis photoisomerization, ϕ_t, of planar stilbenes were recently found to depend very strongly on the viscosity of the medium.[2] The effect was shown to be due to a solvent free volume dependent intramolecular rearrangement process subsequent to the $S_1 \rightarrow T_2$ or $S_1 \rightarrow T_1$ intersystem crossings,[2–4] and the theory[2] for a process of this type

was developed along the lines of the free volume theory of the viscosity of liquids.[5]

In the present paper we wish to describe the results of an investigation of the dependence of the fluorescence quantum yields ϕ_F on the viscosity in a number of nonpolar aromatic compounds.[6] We have observed a

(1) The Weizmann Institute.

(2) D. Gegiou, K. A. Muszkat, and E. Fischer, *J. Amer. Chem. Soc.*, **90**, 12 (1968).

(3) K. A. Muszkat, D. Gegiou, and E. Fischer, *ibid.*, **89**, 4814 (1967).

(4) D. Gegiou, K. A. Muszkat, and E. Fischer, *ibid.*, **90**, 3907 (1968).

(5) (a) M. H. Cohen and D. Turnbull, *J. Chem. Phys.*, **31**, 1164 (1959); (b) D. B. Davies and A. J. Matheson, *ibid.*, **45**, 1000 (1966).

(6) Other investigators have observed effects of viscosity on ϕ_F in the following systems: (a) diphenylmethane dyes, G. Oster and Y. Nishijima, *J. Amer. Chem. Soc.*, **78**, 1581 (1956); (b) tetraphenylbutadienes, M. A. El-Bayoumi and F. M. Abdel-Halim, *J. Chem. Phys.*, **48**, 2536