strong polar (dipole–dipole) solute–solvent interactions. The ketone–hydrocarbon difference in DMF decreases with increasing size, and for a given carbon number decreases in the order cyclic ketones > 2-ketones > symmetrical ketones. $\Delta H(\mathrm{v} \rightarrow \mathrm{Bz})$ and $\Delta H(\mathrm{v} \rightarrow \mathrm{MeOH})$ become less exothermic in this same order. One might be tempted to attribute the large $\Delta H(\mathrm{v} \rightarrow \mathrm{S})$ of cycloalkanones to the smaller molar volumes (by 17–23 mL), but this would not account for the large cycloalkanone–cycloalkane differences, since the cycloalkanes also have smaller volumes than open-chain analogues by about the same amount. However, cycloalkanones have significantly larger dipole moments.[24] $\Delta H(\mathrm{v} \rightarrow \mathrm{MeOH})$ for cyclohexanone is at least 0.5 kcal/mol more exothermic than expected, probably because of partial conversion to the hemiacetal. This is reasonable in view of the much greater reactivity of cyclohexanone (compared with acetone, cyclopentanone, and cycloheptanone) in nucleophilic addition reactions[25] and the greater stability of the resulting addition products.[26] A similar effect has been noted for benzaldehydes with electron-withdrawing substituents.[27] It has also been suggested that the degree of keto–enol tautomerism in various solvents may affect the experimental heats of solution.[14]

While polar interactions of ketones account for the difference in solvation behavior compared with hydrocarbons in MeOH, DMF, and Bz, only for the two simplest ketones do polar interactions contribute more to $\Delta H(\mathrm{v} \rightarrow \mathrm{S})$ than do dispersion forces.

It is interesting to note in Table II that ΔH_s for the ketones in nonpolar DC-200 silicone fluid (measured in connection with GC–calorimetry determinations of ΔH_v) rather closely parallel ΔH_s values in c-C_6, although the values in DC-200 are less endothermic. $\Delta H(\mathrm{v} \rightarrow \mathrm{DC\text{-}200})$ values are correspondingly more exothermic than $\Delta H(\mathrm{v} \rightarrow c\text{-}C_6)$, but less so than for the other solvents.

Acknowledgment. This research was supported by the Robert A. Welch Foundation (Grant E-136).

References and Notes

(1) P. Kebarle in "Ions and Ion-Pairs in Organic Reactions", Vol. I, M. Szwarc, Ed., Wiley-Interscience, New York, 1972, Chapter 2.
(2) P. P. S. Saluja, *MTP Int. Rev. Sci.: Phys. Chem., Ser. Two*, **6**, 1 (1975).
(3) H. Kristenmacher, H. Popkie, and E. Clementi, *J. Chem. Phys.*, **61**, 799 (1974).
(4) R. W. Taft, M. Taagepera, K. D. Summerhays, and J. Mitsky, *J. Am. Chem. Soc.*, **95**, 3811 (1973).
(5) E. M. Arnett, D. E. Jonston, and L. E. Small, *J. Am. Chem. Soc.*, **97**, 5598 (1975).
(6) R. Fuchs and R. F. Rodewald, *J. Am. Chem. Soc.*, **95**, 5897 (1973).
(7) R. Fuchs, T. M. Young, and R. F. Rodewald, *J. Am. Chem. Soc.*, **96**, 4705 (1974).
(8) P. P. S. Saluja, T. M. Young, R. F. Rodewald, F. H. Fuchs, D. Kohli, and R. Fuchs, *J. Am. Chem. Soc.*, **99**, 2949 (1977).
(9) R. Fuchs and P. P. S. Saluja, *Can. J. Chem.*, **54**, 3857 (1976).
(10) The methylene group additivity in hydrocarbons had previously been demonstrated by C. V. Krishnan and H. L. Friedman, *J. Phys. Chem.*, **73**, 1572 (1969); **75**, 3598 (1971).
(11) B. G. Cox, A. J. Parker, and W. E. Waghorne, *J. Am. Chem. Soc.*, **95**, 1010 (1973).
(12) C. Jolicoeur and G. Lacroix, *Can. J. Chem.*, **51**, 3051 (1973).
(13) E. F. Meyer, R. H. Weiss, and T. H. Gens, *J. Chem. Thermodyn.*, **9**, 439 (1977).
(14) W. C. Duer and G. L. Bertrand, *J. Am. Chem. Soc.*, **96**, 1300 (1974); E. L. Taylor and G. L. Bertrand, *J. Solution Chem.*, **3**, 479 (1974).
(15) L. A. Peacock and R. Fuchs, *J. Am. Chem. Soc.*, **99**, 5524 (1977); R. Fuchs and L. A. Peacock, *Can. J. Chem.*, **56**, 2493 (1978).
(16) R. Shaw, *J. Chem. Eng. Data*, **14**, 461 (1969).
(17) S. W. Benson, "Thermochemical Kinetics", 2nd ed., Wiley, New York, 1976.
(18) S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969).
(19) J. L. Hales, E. B. Lees, and D. J. Ruxton, *Trans. Faraday Soc.*, **63**, 1876 (1967).
(20) D. Ambrose, J. H. Ellender, E. B. Lees, C. H. S. Sprake, and R. Townsend, *J. Chem. Thermodyn.*, **7**, 453 (1975).
(21) P. Sellers, *J. Chem. Thermodyn.*, **2**, 211 (1970).
(22) J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, New York, 1970.
(23) E. F. Meyer and R. E. Wagner, *J. Phys. Chem.*, **70**, 3162 (1966).
(24) A. L. McClellan, "Tables of Experimental Dipole Moments", W. H. Freeman, San Francisco, 1963.
(25) H. C. Brown and K. Ichikawa, *Tetrahedron*, 1, 221 (1957); F. P. Price, Jr., and L. P. Hammett, *J. Am. Chem. Soc.*, **63**, 2387 (1941).
(26) V. Prelog and M. Kobelt, *Helv. Chim. Acta*, **32**, 1187 (1949).
(27) R. Fuchs, T. M. Young, and R. F. Rodewald, *Can. J. Chem.*, **51**, 4122 (1973).

Structures and Energies of Cumulene Carbenes

Clifford E. Dykstra,* Craig A. Parsons, and Caren L. Oates

Contribution from the School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801.
Received August 17, 1978

Abstract: Ab initio calculations have been used to predict structures and relative energies of propadienylidene, propargylene, butatrienylidene, ethynylvinylidene, transoid bivinylidene, and diacetylene. Some understanding of the accuracy of the predictions is obtained from extensive SCF and correlated calculations on vinylidene and acetylene. The energies of H_2C_2, H_2C_3, and H_2C_4 cumulene carbenes compared to methylene-like or stable rearrangement structures differ significantly. However, the energies of two different cumulene carbene structures of H_2C_4, butatrienylidene and ethynylvinylidene, are essentially the same. Electron correlation effects on the relative energies were found to be important, but do not change the qualitative predictions from uncorrelated treatments. The method of self-consistent electron pairs (SCEP) was used to determine correlation energies for these large systems and the largest wave function variationally included 120 499 symmetry-adapted configurations.

A recent study of the vinylidene–acetylene rearrangement[1] predicted a rearrangement barrier of 8.6 kcal and an energy difference between vinylidene and acetylene of 40 kcal. For carbenes with cumulene bond systems beyond $H_2C{=}C{:}$, rearrangement products may be stable molecules and also may be other carbenes. If rearrangement barriers for H_2C_3, H_2C_4, etc., are no higher than for vinylidene, these other carbenes may be competitive in radical reaction systems, especially if they are energetically as stable as the cumulene carbene. For a number of reactions involving H_2C_3, it is not clear whether the intermediate carbene is propargylene or propadienylidene.[2] Of the systems in this series of carbenes, vinylidene has been studied the most extensively by ab initio techniques.[1,3-5] Thus, this work was undertaken to determine reasonable structures

0002-7863/79/1501-1962$01.00/0

Table I. Optimized Structures of C_2H_2[a]

	vinylidene			acetylene	
	R_{CH}	R_{CC}	∠HCH	R_{CH}	R_{CC}
DZ/SCF	1.076	1.314	118.7	1.054	1.201
DZ/SCEP[b]	1.096	1.342	117.9	1.071	1.230
DZ + P/SCF	1.079	1.300	120.2	1.060	1.191
DZ + P/SCEP	1.085	1.318	119.7	1.066	1.215
exptl[c]				1.060	1.203

[a] Bond lengths are given in ångstroms and angles are in degrees. [b] From ref 1. [c] R_e values are given, while the corresponding R_0 values are 1.058 and 1.208. (From G. Herzberg, "Molecular Spectra and Molecular Structure", Vol. **III**, Van Nostrand-Reinhold, Princeton, N.J., 1966.)

of H_2CCC: and H_2CCCC: and make a comparison of the relative energies of other carbenes or stable species which might be formed by rearrangement.

Several basis sets were used in the calculations, the smallest of which was a double-ζ (DZ) set of Dunning-contracted[6] Gaussian functions: carbon (9s5p/4s2p) and hydrogen (4s/2s).[7] A DZ + d basis was constructed by supplementing the DZ basis with carbon d functions with an exponent of 0.75. Adding hydrogen p functions, with exponent 1.0, yielded a complete polarization set and this basis is designated DZ + P.

As the simplest member of the series, vinylidene was used to test structural predictions. The recent study of Dykstra and Schaefer[1] included an optimization of the vinylidene structure with the DZ basis and with correlated energies. This was done to maintain a consistent level of treatment in the rearrangement process where correlation may be more important. Their predicted vinylidene C-C bond length was 1.342 Å compared with an SCF result[4] of 1.290 Å. The inclusion of correlation effects is most responsible for the difference.[8] In addition to correlation effects, numerous studies on the simplest carbene, methylene,[9] seem to indicate the importance of d functions on carbon. However, the effect of such polarization functions on geometry predictions is usually an overcontraction of bond lengths[8] at the SCF level. A DZ + P correlated treatment must, therefore, represent a level at which the factors most important to the geometry have not been ignored. This has been clearly demonstrated for triatomics.[10]

Given in Table I are structure predictions for C_2H_2 with DZ and DZ + P basis sets and with and without correlation. Electron correlation was included using the method of self-consistent electron pairs (SCEP).[11,12] The SCEP wave function variationally includes singly and doubly substituted configurations relative to a closed shell reference configuration. Following a recent extension of the method,[13] important quadruple substitutions are included to minimize the size-consistency error. The flexibility of the method makes possible the determination of the large-scale wave functions necessary for this study and the largest reported here (70 basis function, DZ + d, for ethynylvinylidene) spanned a space of over 120 000 symmetry-adapted configurations. Carbon 1s-like orbitals were frozen to substitution in all calculations. The results in Table I show that the greatest differences between DZ + P/SCEP structures are with DZ/SCEP and DZ + P/SCF structures. Because of somewhat of a cancellation of neglected effects, DZ/SCF structures seem to be the most reasonable short of DZ + P/SCEP. Relative energies at a given level of calculation seem to be rather insensitive to the choice of optimized geometries and, as shown in Table II, the range in ΔE values for the various choices of optimized geometries is less than 1.0 kcal for any of the four levels of calculation. Therefore, inclusion of correlation effects or polarization functions has an important effect on relative energies, but variation due to geometry choices are less significant. Also, the DZ/SCF energy difference of 36.0 kcal is closer to the DZ + P/SCEP result of 40.1 kcal than any DZ/SCEP or DZ + P/SCF value (Table II).

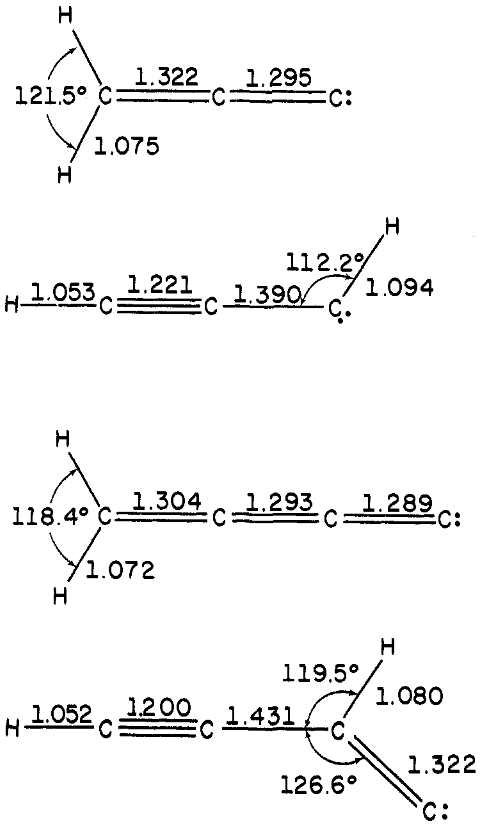


Figure 1. Optimized structures of propadienylidene, propargylene, butatrienylidene, and ethynylvinylidene.

Table II. Energies of C_2H_2

calculation	geometry[a]	$E_{\text{vinylidene}}$, au	$E_{\text{acetylene}}$, au	ΔE, kcal
DZ/SCF		−76.7418	−76.7992	36.0
DZ/SCF[b]	DZ/SCEP	−76.7402	−76.7971	35.7
DZ + d/SCF	DZ + P/SCF	−76.7740	−76.8280	33.9
DZ + P/SCF		−76.7787	−76.8325	33.8
DZ + P/SCF	DZ/SCEP	−76.7759	−76.8293	33.5
DZ + P/SCF	DZ + P/SCEP	−76.7782	−76.8313	33.3
DZ/SCEP[b]		−76.9046	−76.9774	45.7
DZ + P/SCEP	DZ/SCEP	−77.0181	−77.0817	40.0
DZ + P/SCEP		−77.0214	−77.0853	40.1

[a] For some table entries, the calculation was done at a geometry optimized at a different level of calculation. When this was done, the source of the optimized geometry is listed. [b] From ref 1.

Table III. Energies of Cumulene Carbenes and Rearrangement Structures[a]

	DZ basis/SCF		DZ + d basis/SCF		DZ + P basis/SCF		DZ + P basis/SCEP	
	E, au	ΔE, kcal	E, au	ΔE, kcal	E, au	ΔE, kcal	E, au	ΔE, kcal
vinylidene	−76.7418		−76.7737		−76.7784		−77.0214[b]	
acetylene	−76.7992	−36.0	−76.8277	−33.9	−76.8323	−33.8	−77.0853[b]	−40.1
propadienylidene	−114.5602		−114.6079		−114.6117		−114.9577	
propargylene	−114.5387	13.5	−114.5879	12.6	−114.5922	12.2	−114.9318	16.3
butatrienylidene	−152.3908		−152.4504				−152.8809[b]	
ethynylvinylidene	−152.3906	0.1	−152.4525	−1.3			−152.8786[b]	1.4
diacetylene[c]	−152.4596	−43.2	−152.5158	−41.0				

[a] Energies are for systems at their DZ/SCF equilibrium geometries and ΔE's are relative to the cumulene in each set. [b] SCEP energies for H_2C_2 systems are from their DZ + P/SCEP optimum geometries and for H_2C_4 systems the basis was DZ + d. [c] The optimized structure for diacetylene is $R_{C\equiv C}$ = 1.200 Å, $R_{C\text{-}C}$ = 1.388 Å, and $R_{C\text{-}H}$ = 1.052 Å.

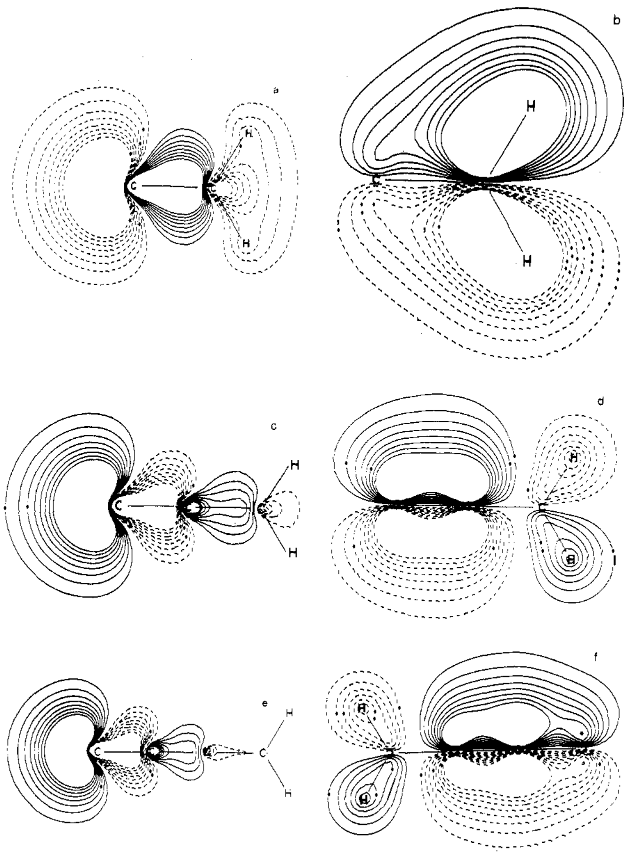


Figure 2. Highest occupied orbitals of the cumulene carbenes: a, $5a_1$ MO of vinylidene; b, $1b_2$ MO of vinylidene; c, $7a_1$ MO of propadienylidene; d, $2b_2$ MO of propadienylidene; e, $9a_1$ MO of butatrienylidene; f, $2b_2$ MO of butatrienylidene.

Singlet electronic states were treated for all of the systems studied. For vinylidene, it has been well established that the ground state is a singlet[1,3,5] and the recent study of Simons et al.[5] shows that larger cumulene carbenes also have singlet ground states. The calculations of Hehre et al.[14] indicate that the ground state of propargylene (or ethynylmethylene) is a triplet state with a different structure than the lowest singlet state. This has not been examined here because the interest is in the rearrangement surface of a vinylidene-like singlet-state carbene. A two-configuration treatment of propargylene may be appropriate, by analogy with singlet methylene,[9] but at the uncorrelated level this introduces an inequivalency in the treatment of the two H_2C_3 structures. In the correlated treatment of H_2C_3, the inclusion of quadruple substitutions overcomes some part of the inequivalency error since important double substitutions with respect to a second configuration are implicitly included.

Table IV. Orbital Occupancies

propadienylidene	$1a_1^2\ 2a_1^2\ 3a_1^2\ 4a_1^2\ 5a_1^2\ 6a_1^2\ 1b_2^2\ 1b_1^2\ 7a_1^2\ 2b_2^2$
propargylene	$1a'^2\ 2a'^2\ 3a'^2\ 4a'^2\ 5a'^2\ 6a'^2\ 7a'^2\ 8a'^2\ 1a''^2\ 9a'^2$
butatrienylidene	$1a_1^2\ 2a_1^2\ 3a_1^2\ 4a_1^2\ 5a_1^2\ 6a_1^2\ 7a_1^2\ 8a_1^2\ 1b_2^2\ 1b_1^2\ 9a_1^2\ 2b_2^2\ 1b_1^2$
ethynylvinylidene	$1a'^2\ 2a'^2\ 3a'^2\ 4a'^2\ 5a'^2\ 6a'^2\ 7a'^2\ 8a'^2\ 9a'^2\ 1a''^2\ 10a'^2\ 11a'^2\ 2a''^2$
transoid bivinylidene	$1a_g^2\ 1b_u^2\ 2a_g^2\ 2b_u^2\ 3a_g^2\ 3b_u^2\ 4a_g^2\ 4b_u^2\ 5a_g^2\ 1a_u^2\ 5b_u^2\ 6a_g^2\ 1b_g^2$
diacetylene	$1\sigma_g^2\ 1\sigma_u^2\ 2\sigma_g^2\ 2\sigma_u^2\ 3\sigma_g^2\ 3\sigma_u^2\ 4\sigma_g^2\ 4\sigma_u^2\ 5\sigma_g^2\ 1\pi_u^4\ 1\pi_g^4$

Table V. Dipole Moments of Cumulene Carbenes[a]

	SCF	SCEP
vinylidene	2.30	2.31
propadienylidene	4.29	4.19
butatrienylidene	4.53	4.55

[a] In debyes; DZ + d or DZ + P basis sets used.

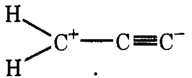
The carbene H_2C_3 and H_2C_4 structures, optimized at the DZ/SCF level, are given in Figure 1 and their energies are in Table III. Molecular orbital occupancies are listed in Table IV. For H_2C_3, the predicted geometries are similar to those obtained by Hehre et al.[14] at the STO-3G/SCF level. Their carbon-carbon bond lengths were slightly shorter than we obtained with a DZ basis, but the difference between the two C-C bond lengths in propadienylidene is essentially the same as their result. For propargylene, Hehre et al.[14] made the interesting prediction that the acetylene system was slightly trans distorted. We did not find this in our optimization; however, the magnitude of distortion which they predicted was small (<5°) and thus our results are basically in agreement.

The importance of basis set size on relative energies of H_2C_3 structures was well established by the calculations with various basis sets performed by Hehre et al.[14] For instance, at the STO-3G level they found propadienylidene to be about 8.0 kcal more stable than singlet propargylene, while with a 4-31G basis this energy difference nearly doubled. The energies in Table III seem to indicate that adding polarization functions to the basis may change relative energies by a few kilocalories. Inclusion of electron correlation, on the other hand, tends to balance these changes. The effect of hydrogen p polarization functions is very small and, therefore, these functions were not included in the H_2C_4 systems.

The most interesting result in Table III is that butatrienylidene is almost exactly as stable as its rearranged carbene, ethynylvinylidene. Also, the energy difference between these forms and the stable structure, diacetylene, is similar to the energy difference between vinylidene and acetylene. The energy for forming a cumulene carbene thus seems rather independent of the molecular structure after the first two carbons

$>C{=}C:$ of the carbene. (The H_2C_3 results, of course, show significant energy differences between cumulene and methylene carbene forms.) As a further test of this qualitative carbene formation energy independence, the structure of transoid bivinylidene was optimized at the DZ/SCF level: $R_{CH} = 1.077$ Å, $R_{C{=}C:} = 1.320$ Å, $R_{C\text{-}C} = 1.470$ Å, $\angle CCC = 125.7°$, and $\angle C\text{-}C\text{-}H = 119.8°$. The DZ/SCF energy of this is -152.3265 au or about 83.5 kcal above diacetylene. This is roughly twice the vinylidene-acetylene energy difference, again suggesting that the energy to form a cumulene carbene has only a small dependence on the rest of the molecule's structure.

Dipole moments for the cumulene carbenes are given in Table V. In agreement with Hehre et al.[14] we find a dipole moment for propadienylidene of around 4 D. Interestingly, correlation effects on the dipole moment are small, which is in part due to the dominance of the SCF reference configuration in the correlated wave function. The dipole moment for butatrienylidene is almost the same as for propadienylidene. The stabilization of a cumulene carbene through charge separation proposed by Hehre et al.[14] for H_2C_3 and represented



i

as i is most favorable when there is an odd number of carbons in the cumulene system. Thus, the dipole moment changes significantly in going from vinylidene to propadienylidene and likewise may be expected to change when going from H_2C_4 to H_2C_5.

Finally, presented in Figures 2a-f are the highest a_1 and b_2 occupied orbitals for the three cumulene carbenes.[15] Some preliminary idea of rearrangement barriers may be obtained by examining the nodal structures of the orbitals. For vinylidene, there is a node in the a_1 orbital perpendicular to the carbon axis around the methylene carbon, but there is no node for the b_2 orbital. The barrier for moving one of the two vinylidene hydrogens toward the other carbon is 8.6 kcal.[1] For both H_2C_3 and H_2C_4, the highest b_2 orbital is the $2b_2$ and, unlike the vinylidene $1b_2$ orbital, there is a node around the methylene carbon. This suggests a larger rearrangement barrier for propadienylidene and butatrienylidene than vinylidene.

Acknowledgments. We thank Dr. Leo Radom for his helpful comments. We thank Dr. A. J. Arduengo for making available to us modifications of W. L. Jorgensen's plotting program.[15] The donors of the Petroleum Research Fund, administered by the American Chemical Society, are gratefully acknowledged for support of this work. Computer time was provided by the University of Illinois Research Board.

References and Notes

(1) C. E. Dykstra and H. F. Schaefer, *J. Am. Chem. Soc.*, **100**, 1378 (1978).
(2) H. D. Hartzler in "Carbenes", Vol. 2, R. A. Moss and M. Jones, Eds., Wiley-Interscience, New York, 1975.
(3) J. H. Davis, W. A. Goddard, and L. B. Harding, *J. Am. Chem. Soc.*, **99**, 2919 (1977).
(4) A. C. Hopkinson, K. Yates, and I. G. Csizmadia, *J. Chem. Phys.*, **55**, 3835 (1971).
(5) J. W. Kenney, J. Simons, G. D. Purvis, and R. J. Bartlett, *J. Am. Chem. Soc.*, **100**, 6930 (1978).
(6) T. H. Dunning, *J. Chem. Phys.*, **53**, 2823 (1970).
(7) For H_2C_3 and H_2C_4 a slightly better hydrogen basis of three functions (5s/3s) was used. The first three primitive functions were contracted into one basis function using atomic orbital coefficients given by S. Huzinaga, *J. Chem. Phys.*, **42**, 1293 (1965).
(8) H. F. Schaefer, "The Electronic Structure of Atoms and Molecules", Addison-Wesley, Reading, Mass., 1972.
(9) Among the recent studies of CH_2 are L. B. Harding and W. A. Goddard, *J. Chem. Phys.*, **67**, 1777 (1977); R. R. Lucchese and H. F. Schaefer, *J. Am. Chem. Soc.*, **99**, 6765 (1977); C. W. Bauschlicher and I. Shavitt, *ibid.*, **100**, 739 (1978); B. Roos and P. Siegbahn, *ibid.*, **99**, 7716 (1977); L. B. Harding and W. A. Goddard, *Chem. Phys. Lett.*, **55**, 217 (1978); S.-K. Shih, S. D. Peyerimhoff, R. J. Buenker, and M. Peric, *ibid.*, **55**, 206 (1978).
(10) S. Bell, *J. Chem. Phys.*, **68**, 3014 (1978).
(11) C. E. Dykstra, H. F. Schaefer, and W. Meyer, *J. Chem. Phys.*, **65**, 2740, 5141 (1976).
(12) C. E. Dykstra, QCPE, Vol. 10, 1978, program 346.
(13) C. E. Dykstra, *J. Chem. Phys.*, **68**, 1829 (1978).
(14) W. J. Hehre, J. A. Pople, W. A. Lathan, L. Radom, E. Wasserman, and Z. R. Wasserman, *J. Am. Chem. Soc.*, **98**, 4378 (1976).
(15) W. L. Jorgensen, QCPE, Vol. 10, 1977, program 340.

An Amplified Sector Rule for Electric Dipole-Allowed Transitions[1]

Oscar E. Weigang, Jr.

Contribution from the Department of Chemistry, University of Maine at Orono, Orono, Maine 04469. *Received May 22, 1978*

Abstract: A sector rule based on electron correlation or "dynamic coupling" between the chromophore and bonds of a molecule is developed for electric dipole-allowed transitions. In its simplest form, the development corresponds to a quantum model of rotatory strength arising from coupled electric dipole oscillators. With the rule, the sign and magnitude of transition rotatory strength can be estimated by examining a molecular model. Only knowledge of the transition wavelength and direction of polarization is required. Unlike most sector rules, it is necessary to observe carefully the orientation as well as the location of bonds placed dissymmetrically with respect to the chromophore. A number of illustrations are given for the butadiene 260-nm, the ketone 190-nm, and the ethylene 190-nm transitions. It appears that a "resonance" of the carbon-carbon bond polarizability perpendicular to the usually dominant polarizability along the bond occurs somewhere between 260 and 200 nm.

The Rosenfeld expression for rotatory strength:

$$R_{NK} = \mathrm{Im}\{\boldsymbol{\mu}_{NK} \cdot \mathbf{m}_{KN}\} \qquad (1)$$

defines the leading term, according to quantum mechanics, for the origin of optical activity in absorption band K ← N. The vector $\boldsymbol{\mu}_{NK}$ is the electric dipole transition moment and $\mathbf{m}_{KN}$ the magnetic dipole transition moment on going from state N to state K. The expression, correct to the dipole level of interaction between the light field and the molecule, is otherwise completely general. It assumes that molecular wave functions $|N\rangle$ and $|K\rangle$, with matrix elements that lead to suitably oriented dipoles $\boldsymbol{\mu}_{NK}$ and $\mathbf{m}_{KN}$, are sufficiently complete descriptions of the molecular system.

0002-7863/79/1501-1965$01.00/0