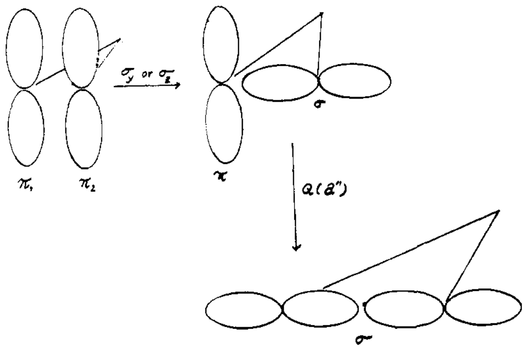

Figure 21. An alternate view of the pathways XI and XII.

destroyed. This implies that the promoting mode cannot belong to any single symmetry species of C_{2v}. Two assumptions need be examined. If the reaction is assumed to proceed to completion in one step, the violation of the C_{2v} selection rule forces us to consider the smaller C_1 trivial group. No useful information can be derived. If more steps are involved, it is conceivable that there might be involved a b_2-type motion corresponding to the hydrogen migration from the central carbon to one of the two terminal carbons, and a b_1-type motion of the other hydrogen atom attached to the central carbon, bringing itself into the C-C-C plane. The required spin inversion may take place simultaneously or separately because of the selection rules II, III, and IV. At any rate, as far as the second-order perturbation theory is concerned, the second assumption is disfavored.

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(27) The same as ref 25.

The Electronic Structure of Methylene Radical Anion and Its Dimer

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Abstract: Nonempirical molecular orbital calculations are used to construct a Walsh diagram for methylene radical anion, CH_2^-; the best 4-31G calculation done gives $E_T = -38.7814$ hartrees at $r_{CH} = 1.145$ Å and $\theta_{HCH} = 99°$. The effects of various model substituents on the carbanion-like σ lone pair and on the free radical-like odd p electron of the central carbon atom are explored in a series of CNDO/2 semiempirical molecular orbital calculations. These suggest that good π acceptor substituents will narrow or even reverse the gap between the two valence orbitals, providing an opportunity to manipulate reactivity. The dimer of CH_2^-, which has been suggested as an intermediate in the production of ethylene from the monomer, is examined in another series of nonempirical SCF calculations. They indicate that the dimer lies in a metastable local minimum of the potential energy hypersurface for the dimerization reaction; the lowest calculated 4-31G energy is -77.4203 hartrees. The calculations are used to discuss related experimental data.

The intriguing, highly reactive species CH_2^-, the radical anion of methylene, seems to be produced in surprising abundance when methylene halides are treated with strong reducing agents in solution;[1] the same ion has been prepared in the gas phase by electric discharges in CH_4 or CH_2N_2.[2] The novelty of this molecule, its potential for reactivity characteristic of either free radical or carbanionic functionality, and the possibility of its dimerization in solution to form the dianion of ethylene[1] led us to study its electronic structure (and that of its dimer) in a series of molecular orbital calculations.

The corresponding neutral species, CH_2, has been exhaustively examined, both theoretically[3] and experimentally.[4] It is especially interesting to the theorist because it is the archetypal diradical:[5] a molecule in which the presence of two electrons to be distributed among two nearly degenerate orbitals produces an exquisite sensitivity to geometric change and substitution.[6] The extra electron in CH_2^- removes some of the interesting ambiguity in the assignment of ground state configuration but simultaneously alters the delicate balance of orbital energies which determines structure and reactivity in

Table I. Calculated and Experimental Geometries of Species Related to CH_2^-

Species	State	CNDO/2 r_{eq}[b]	CNDO/2 θ_{HXH}[c]	CNDO/2 E_{total}[d]	SCF[a] r_{eq}[e]	SCF[a] θ_{HXH}[f]	SCF[a] E_{total}[g]	Exptl r[b]	Exptl θ[c]
CH_2	$^3B_1$	1.094	141.9	−220.074	1.082	125.5	−1057.683	1.078[h]	136.0[h]
CH_2	$^1A_1$	1.111	108.0	−221.664	1.123	100.5	−1056.064	1.12[i]	103.2[i]
NH_2	$^2B_1$	1.064	105.6	−352.567	1.058	100.2	−1509.453	1.024[j]	103.3[j]

[a] Calculations reported in ref 9. [b] Ångströms. [c] Degrees. [d] Electron volts (valence electrons only). [e] Ångströms; from STO-3G calculations (ref 10). [f] Degrees; from STO-3G calculations. [g] Electron volts; from 4-31G calculations (ref 11); converted using 1 hartree = 27.211 608 eV from E. R. Cohen and B. N. Taylor, *J. Phys. Chem. Ref. Data,* **2,** 663 (1973). [h] G. Herzberg and J. W. C. Johns, *J. Chem. Phys.,* **54,** 2276 (1971). [i] G. Herzberg, *Proc. R. Soc. London, Ser. A,* **262,** 291 (1961). [j] K. Dressler and D. A. Ramsay, *Philos. Trans. R. Soc. London, Ser. A,* **251,** 553 (1959).

this system. In examining that balance using molecular orbital arguments and calculations, it must be remembered that serious difficulties may be encountered[7] when negative ions are treated using the usual orbital approximations.[8] In particular, valence electrons of the molecule may have positive one-electron energies, indicating that a system with one or more of those electrons detached might be more stable.

We have nonetheless chosen to use this type of calculation, for two reasons. First, one of the most useful attributes of theoretical models is that they facilitate the examination of systems in extraordinary conditions. Chemical reactions often produce molecules in nonequilibrium, high-energy states and the fact that they rapidly decay in one way or another does not make them uninteresting. In the present case, a negative ion might, if it were produced in isolation, eject one or more electrons almost instantaneously; a description wherein those electrons are constrained to be bound is nonetheless useful because it provides a much better reference point for discussion of similar ions stabilized by counterions or solvation than a (lower energy) wave function in which some of the electrons have been removed. Second (and perhaps more important), there are strong indications that Nature does not consider herself constrained by the predictions of small basis set Roothaan-Hartree-Fock calculations. The positive orbital energies may become negative when larger basis sets are used[7c,d] or it may happen, especially in cases where positive one-electron energies are small, that the actual molecule holds its Hartree-Fock-unbound electrons, though such a molecule would most likely be a moderately strong reducing agent. Despite the positive one-electron energies in our SCF calculations on CH_2^-, its experimental observation[2] leads us to believe that it, at least, is worth studying.

Two types of calculations are used in this work. The parent methylene radical ion and its dimer were examined in a series of nonempirical MO-SCF calculations[8a] using modest basis sets of Gaussian functions (the unrestricted Hartree-Fock form[8b] is used for the CH_2^- wave function). In a procedure developed by Pople and co-workers,[9] geometry optimization is carried out using three-Gaussian simulations of the Slater orbitals of a minimal basis set (the exponents are partially optimized for molecular environments[10]). When the geometry search is completed, a more flexible basis set,[11] wherein each Slater orbital is represented by four Gaussian functions, is employed to calculate a better wave function with a lower total energy. Most of the improvement comes from splitting the most diffuse component of each valence orbital from the others and allowing its contribution to the molecular orbitals to be determined separately by the variational process. All the nonempirical SCF calculations were carried out using a modified version of the Gaussian 70 program available from the Quantum Chemistry Program Exchange.[12] To examine the effects of substitution on the geometry and electronic structure of CH_2^-, approximate SCF calculations of the CNDO type[13,14] are used to allow the examination of larger systems. The wave functions calculated in this part of the study are of the restricted Hartree-Fock variety and are obtained using the "half-electron" formalism.[16] All reported orbital energies and wave functions were obtained from calculations at optimized geometries. That the calculations provide a reasonable description of molecules similar to those examined here is indicated by Table I.[17]

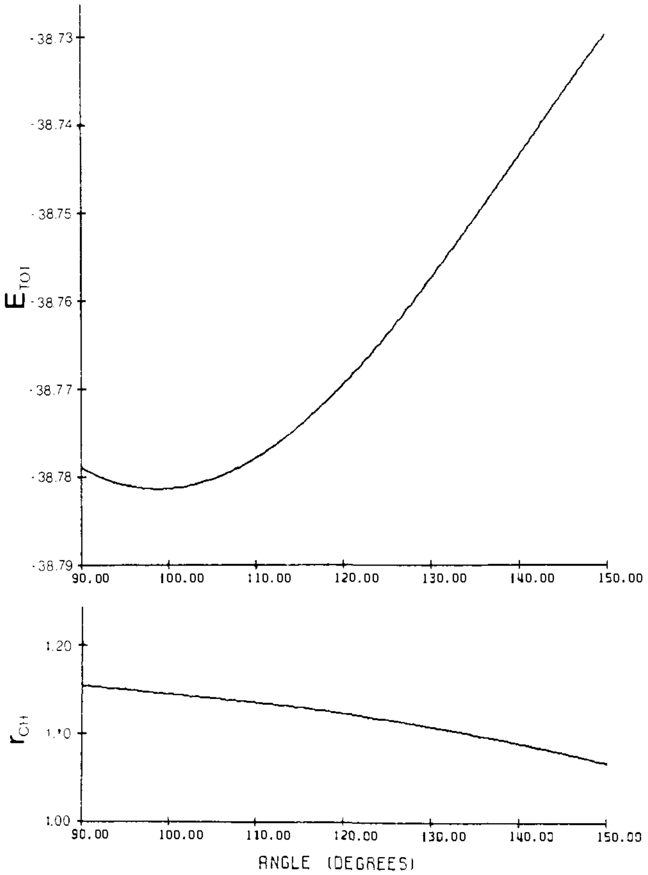

Figure 1. Total energy (hartrees) and equilibrium CH bond length (Å) for methylene radical anion, CH^-. Bond lengths from STO-3G calculations; energies from 4-31G calculations.

Methylene Radical Anion

Despite its ionic character, the calculations show that the parent species, CH_2^-, is in many ways a typical nine-electron AH_2 molecule. Its equilibrium CH bond length (as determined by STO-3G calculations[10]) and its total energy (as determined by 4-31G calculations[11] at the STO-3G bond lengths) are smooth functions of the HCH angle; the dependence is shown in Figure 1. The 99° calculated equilibrium angle (at which $E_T = -38.7814$ hartrees and $r_{CH} = 1.145$ Å) agrees quite well with the estimated experimental value[2] of 99 ± 3° and may, in the spirit of Walsh,[19] be attributed to balancing of the tendency of the b_2 orbital labeled CH-CH in Figure 2 to minimize

Table II. One-Electron Energies (eV) and Electron Populations for Substituted Methylene Radical Anions ($X-C-Y^-$)

X	Y	$\epsilon(\sigma)$	$\epsilon(p)$	$\Delta\epsilon$	$P_\sigma{}^C$(valence[c])	$P_p{}^C$(valence[c])	$P_\sigma{}^C$(total)	$P_p{}^C$(total)
H	H	−1.1325	0.8844	2.0	1.736	1.000	3.653	1.000
H	F	−1.3749	1.2332	2.6	1.383	0.912	3.415	1.088
F	F	−2.9600	1.4555	4.4	1.377	0.851	3.217	1.149
H	OH	−1.0428	1.8098	2.9	1.381	0.876	3.435	1.124
H	NH_2	−1.3982	1.9223	3.3	1.315	0.658	3.562	0.961
H	CH_3	−2.0399	0.6920	2.7	1.396	0.670	3.673	0.872
CH_3	CH_3	−2.0475	0.1074	2.2	1.302	0.570	3.610	0.875
H	CHO	−0.9565	−2.4670	1.5	0.579[a]	0.741[b]	3.140	1.294

[a] Singly occupied. [b] Doubly occupied. [c] As in the text, the term valence refers to the frontier HDOMO and HSOMO. Except when the substituent is CHO, the former is the orbital labeled σ in Figure 2 and the latter is the orbital labeled p in Figure 2.

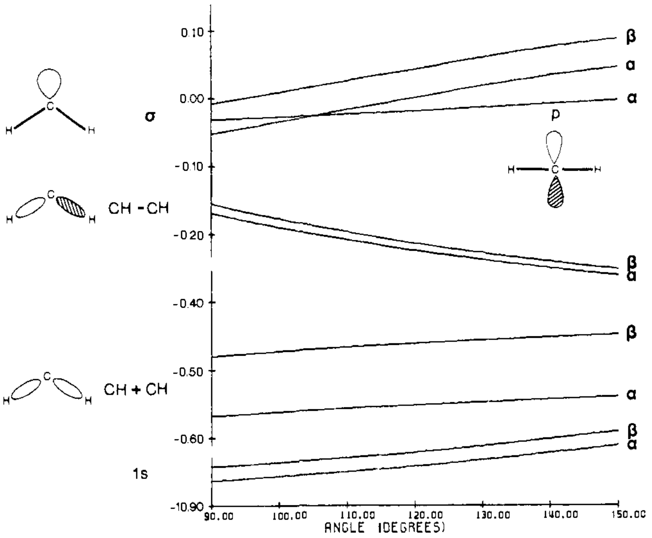

Figure 2. Orbital energies (electron volts) vs. HCH angle for CH_2^- from 4-31G calculations.

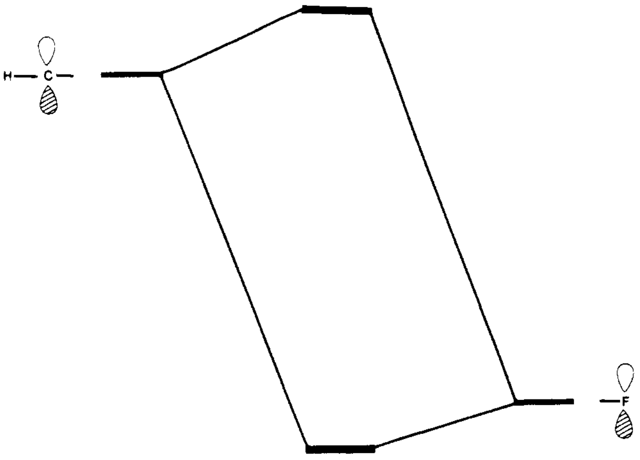

Figure 3. Interaction of out-of-plane central carbon p orbital with fluorine p orbital of appropriate symmetry.

the antibonding interaction between the terminal hydrogens by opening the angle and the tendency of the a_1 orbital labeled σ in Figure 2 to maximize its electrons' s character by closing the angle. The "extra" electron in the b_1 orbital labeled p in Figure 2 is, as might be expected, relatively insensitive to the HCH angle; as a result, the calculated size of that angle is found to be quite close to the calculated value of the corresponding angle in the lowest $^1A_1$ state of CH_2, which, except for the "extra" electron, has an identical configuration. In fact, the Walsh diagram for CH_2^- is, aside from small quantitative changes which arise from shifts of electron density from carbon to hydrogen in the low-lying orbitals, almost identical with that for CH_2.[3b]

Substituent Effects

Our primary interest is in the reactivity of carbene radical anions, and particularly in the competition between free-radical reactivity involving the unpaired p electron and carbanion reactivity involving the paired electrons in the orbital labeled σ in Figure 2. We therefore focus on the effects of model substituents on these two valence (frontier[20]) orbitals in discussing our CNDO/2 calculations. A very simple substituent, fluorine, illustrates the interactions which must be considered in predicting and understanding the effects of more complex substitution. As shown in Figure 3, the p orbital of CH_2^- interacts with an out-of-plane p orbital of fluorine to form a low-energy in-phase combination, delocalizing one of the fluorine lone pairs somewhat onto carbon, and a high-energy out-of-phase combination, delocalizing the unpaired electron of the highest (singly) occupied molecular orbital (HSOMO) somewhat onto fluorine. The significant net results of this interaction are donation of the π electron density from fluorine to carbon (via the fluorine lone pair orbital which is the HSOMO's interaction partner) and elevation of the HSOMO's energy; this can be seen in Table II. An exactly similar argument can be made for π interactions in the difluoro ion, with the in-phase combination of out-of-plane fluorine p orbitals replacing the single fluorine orbital in the interaction scheme; each of the effects identified in that discussion is somewhat amplified (see Table II).

The effects of fluorine substitution on the highest doubly occupied molecular orbital (HDOMO) are more complicated because there are many more orbitals which interact; in CF_2^-, starting with the usual chemist's semilocalized picture, interactions of σ with two fluorine lone pair combinations, with the in-phase combination of carbon-fluorine bond orbitals, and with the in-phase combination of unoccupied carbon-fluorine antibond orbitals must be considered. Though less satisfying than the qualitative arguments of the previous discussion, the SCF procedure gives us the result of all these interactions; admixture of low-energy fluorine orbitals stabilizes each of the orbitals of σ symmetry relative to their counterparts in the parent compound by withdrawing carbon σ electrons (mostly from in-plane p orbitals) to more electronegative fluorine. This is reflected in the total carbon sigma electron population as well as in the HSOMO sigma population. The raising of HSOMO energy and lowering of HDOMO energy by fluorine substitution imply that fluoromethylene radical anions are more likely to undergo free-radical reactions like coupling (vide infra) and less likely to undergo carbanionic reactions, like proton abstraction from solvent and nucleophilic displacement, than the parent ion. Calculations indicate that other π donor-σ acceptor substituents, e.g., OH and NH_2 (see Table II), have similar effects; were the appropriate starting materials to

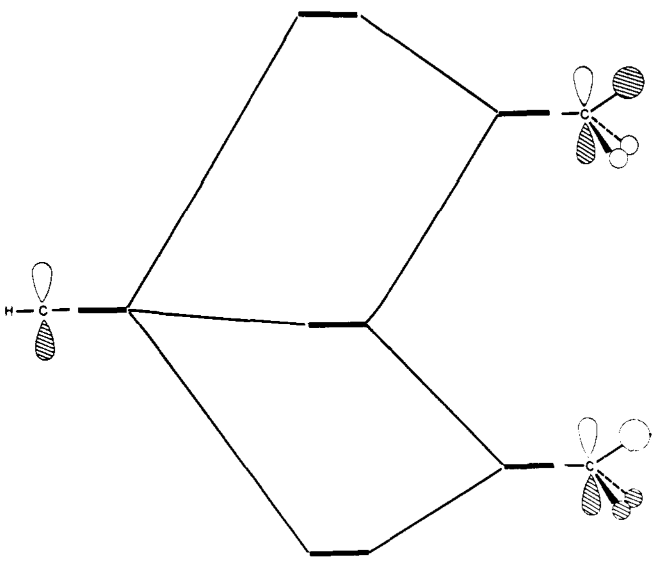

Figure 4. Interaction of central carbon p orbital with methyl group orbitals.

survive the strongly reducing conditions under which the radical anions are usually produced, similar predictions of reactivity would apply.

No profound structural changes accompany the introduction of fluorine substituents. There are such changes, however, when methyl groups are substituted for hydrogen. In these CNDO/2 calculations CH_2^- has an equilibrium HCH angle of 105°. The CHF^- and CF_2^- central angles (106 and 104°, respectively) deviate only slightly from that value. In $CHCH_3^-$ and $C(CH_3)_2^-$, the central angles open to 113 and 124°, respectively, reflecting the greater steric requirements of CH_3 (exaggerated, it seems, in NDO calculations[21]). The electronic effect of methyl groups is to withdraw electron density from carbon via the π system[22] but to leave the total carbon σ charge unchanged. As shown in Figure 4, the parent ion p orbital interacts with both an occupied bonding group orbital and an unoccupied antibonding group orbital of methyl, the net result being a lowering of the HSOMO one-electron energy and delocalization of the HSOMO electron into CH_3. As was the case with fluorine substitution, two methyls accentuate the change in one-electron energy and central carbon p populations. Interactions with the parent ion σ orbital are again more complex than those with the p orbital; the net effect is delocalization of the HDOMO from central carbon to methyl (comparable in magnitude to the corresponding σ withdrawal by fluorine!) and a fairly large reduction in the HDOMO one-electron energy. When a second methyl group is added, it affects the σ orbital hardly at all; as a result, the energy gap between HSOMO and HDOMO, which had been increased with the first CH_3 lowered HDOMO more than it lowered HSOMO, is reduced when HSOMO is lowered further still and HDOMO is unchanged. Correspondingly, $CHCH_3^-$ ought to be slightly less likely than CH_2^- to react as a carbanion rather than as a radical and $C(CH_3)_2^-$ ought to display reactivities similar to those of CH_2^-.

In order to increase carbanion reactivity, substituents should be chosen which narrow the gap between the HSOMO and the HDOMO. The arguments and calculations above suggest that this might be accomplished with a π acceptor substituent which does not simultaneously lower the energy of the parent ion σ orbital dramatically. The formyl group seemed a likely model for such substituents and calculations were performed on the $CHCHO^-$ ion. The formyl group has a low-lying π^* orbital, concentrated on carbon, which, when it interacts with the p orbital of the parent ion, should lower the latter's energy. The C=O π orbital, which would raise the energy of the orbital of interest, is concentrated on oxygen and thus interacts less strongly with adjacent π systems. These expectations are summarized in Figure 5. When the calculations were done (see Table II) the gap did, in fact, decrease to the lowest value for any of the ions so far studied. The gap might have been smaller still had our strategem not worked too well! Interaction with the formyl π^* orbital lowered the parent ion p orbital *below* the parent ion σ, making p the HDOMO ("carbanion" orbital) and σ the HSOMO ("radical" orbital). The calculations are not sufficiently reliable to predict with confidence that this would happen experimentally, but the result does suggest that a promising approach to more carbanion-like carbene radical anions is the production of ions with formyl, cyano, or other π acceptor substituents.

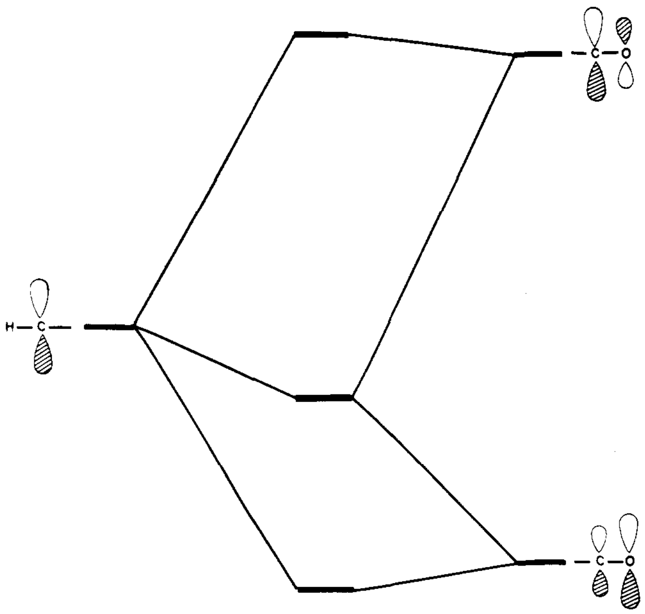

Figure 5. Interaction of central carbon p orbital with formyl group carbonyl π orbitals.

The Dimer of CH_2^-

When Sargent postulated a dimerization of CH_2^- to the dianion of ethylene in a sequence leading to the neutral form of the latter, it was with some misgivings about the plausibility of such a postulate.[1] The data do not require the dimer's intermediacy, but they are explained most satisfactorily that way. Moreover, the tetraphenylethylene dianion is a well-known species[24] which has been produced in environments not very dissimilar to those of Sargent's experiments. As a test of the plausibility of the dimerization postulate, it seemed useful to examine the species in a series of SCF calculations to see if it corresponds at least to a metastable intermediate, a local minimum on a hypothetical reaction surface, with energy barriers to dissociation or gross rearrangement. At an initial value of the dihedral angle (labeled ϕ in Figure 6), the carbon-carbon bond length, the carbon-hydrogen bond length, the HCH angle, and the "flap" angle α were adjusted to minimize the STO-3G calculated energy. Thereafter, only the flap angle was reoptimized at each dihedral angle. Finally, the energy was recalculated at each dihedral angle using the partially optimized geometry and the 4-31G basis set (because comparison of the torsional potential with that of similar "normal" molecules such as hydrazine[25] is of some interest and because that geometric variable is expected to be especially sensitive to basis set flexibility); the calculated energies are plotted in Figure 7. At least in these calculations, the dianion *is* a metastable species;[26] the "equilibrium" structure, with

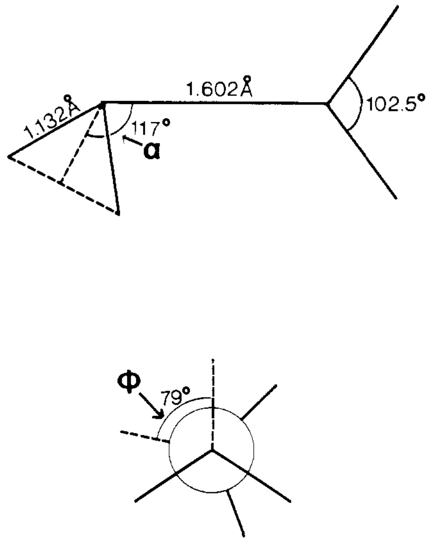

Figure 6. Equilibrium geometry of ethylene dianion from STO-3G calculations. Dihedral angle interpolated from 4-31G calculations at STO-3G geometries.

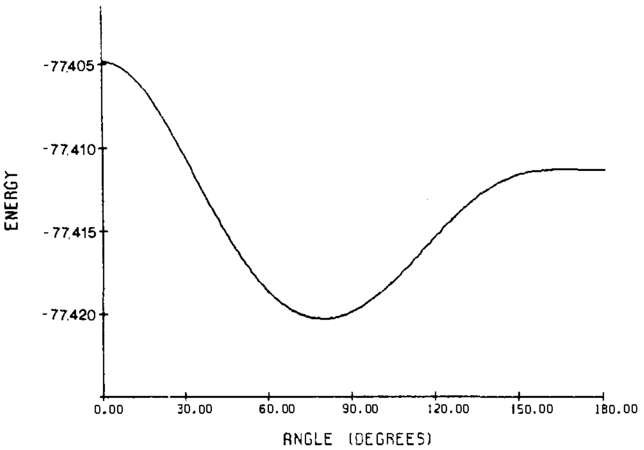

Figure 7. Total energy (hartrees) vs. dihedral angle for ethylene dianion from 4-31G calculations at STO-3G geometries.

4-31G energy −77.4203 hartrees, is indicated in Figure 6. As expected, however, the ion has a very strong tendency to lose electrons: both the "lone pair" orbitals (corresponding to the π and π^* orbitals of neutral ethylene) had large positive one-electron energies at all dihedral angles. The calculations lend credence to the possibility that two methylene radical anions *could* come together to form a dimer (with some activation energy), which would immediately lose the two "extra" electrons (much more easily than the monomeric anions).

Conclusions

The methylene radical anion is an ordinary nine-electron AH_2 molecule with a geometry very much like that of the lowest singlet state of the neutral parent species. The "extra" electron is loosely held, but the molecule is stable against various types of distortion. The unpaired electron is contained in an out-of-plane carbon p orbital; the interactions of that p orbital with adjacent substituents are quite predictable and can be used to alter the relative energies of the valence orbitals of the ion. The dimer of CH_2^-, the dianion of ethylene, is also stable to moderate geometric distortions according to these calculations. It ought to lose its two "extra" electrons extremely easily, much more easily than the monomer. In light of these calculations, a scenario wherein two methylene radical anions (possibly stabilized by counterions) dimerize to form the dianion of ethylene (again stabilized by counterions), which almost immediately loses two electrons to the environment, seems quite reasonable.

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(16) M. J. S. Dewar, J. A. Hashmall, and C. G. Venier, *J. Am. Chem. Soc.*, **90**, 1953 (1968); M. J. S. Dewar and N. Trinajstić, *J. Chem. Soc. A*, 1220 (1971). The orbital energy of the odd electron does not appear as an eigenvalue in this scheme; it was calculated explicitly (see ref 8a).

(17) The incorrect ordering of the $^3B_1$ and $^1A_1$ states of CH_2 arises in large part from the neglect of one-center exchange integrals which stabilize unpaired atomic electrons. Such integrals, which are included in INDO calculations, profoundly affect spin properties (including the relative energies of different states arising from the same configuration) but do not change either geometry or charge distribution very much (ref 18).

(18) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill, New York, N.Y., 1970, pp 95–97.

(19) A. D. Walsh, *J. Chem. Soc.*, 2260 (1953).

(20) The decisive importance of valence orbitals of molecules in reactivity has been emphasized by Fukui. See, for example, K. Fukui, *Fortsch. Chem. Forsch.*, **15**, 1 (1970).

(21) W. J. Hehre, *J. Am. Chem. Soc.*, **97**, 5308 (1975).

(22) The notion that, in the absence of solvent, methyl groups act primarily as polarizable stabilizers of either positive or negative charge rather than inflexible electron donors is now well established (ref 23).

(23) (a) J. I. Brauman and L. K. Blair, *J. Am. Chem. Soc.*, **92**, 5986 (1970); (b) J. I. Brauman and L. K. Blair, *ibid.*, **93**, 3911 (1971); (c) J. I. Brauman, J. M. Riveros, and L. K. Blair, *ibid.*, **93**, 3914 (1971).

(24) See J. F. Garst, *J. Am. Chem. Soc.*, **93**, 6312 (1971), for references. The substituent phenyl groups undoubtedly stabilize this dianion; it is equally likely that they stabilize the monomeric anions. Their net effect on the dimerization reaction cannot be predicted a priori.

(25) J. O. Jarvie and A. Rauk, *Can. J. Chem.*, **52**, 2785 (1974), and references therein.

(26) In the optimization of the carbon–carbon bond length, elongations of a few tenths of an ångström typically led to energy increases of more than 20 kcal/mol. Part or all of this may be the result of the well-known incorrect dissociation behavior of restricted Hartree–Fock wave functions. It may be, however, that this problem is less serious for this dianion, where the

overemphasized canonical structures are a dianion and a neutral, than it is for an uncharged closed shell molecule, where the offending positive and negative structures have a strong coulombic attraction. It might also be argued that electron correlation is likely to be much more important in lowering the energy of the dianion than it is in the dissociation products, increasing the likelihood that the dianion might have a finite lifetime. We are grateful to the referees, who were of opposite opinions on this point, for encouraging us to discuss it.

Spectroscopy, Photophysics, and Photochemistry of Dimethyl-*s*-tetrazine and Phenyl-*s*-tetrazine in Crystals and Mixed Crystals at Low Temperatures

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Abstract: The electronic absorption, fluorescence, and phosphorescence spectra of dimethyl-*s*-tetrazine and phenyl-*s*-tetrazine at low temperatures (4.2–1.6 K) are reported and analyzed in the neat and mixed crystal. The S_1–S_0 spectral origin is at 17 352 cm^{-1} for neat dimethyl-*s*-tetrazine, 17 659 cm^{-1} for neat phenyl-*s*-tetrazine, 17 001 cm^{-1} for dimethyl-*s*-tetrazine in *p*-xylene, and 17 167 cm^{-1} for phenyl-*s*-tetrazine in benzophenone; the neat crystal T_1–S_0 origin is at 13 079 cm^{-1} for dimethyl-*s*-tetrazine and 13 333 cm^{-1} for phenyl-*s*-tetrazine. The observed spectra were characteristic of symmetry allowed n–π* transitions and correspond to the *s*-tetrazine $^{1,3}B_{3u}$–^1A_g (nπ*) transitions. Several progression forming modes were observed. The vibrational frequency in the ground state S_0 (and in the S_1 excited state in parentheses) for the methyl torsion designated X is 50 cm^{-1} (49 cm^{-1}) and the ring breathing mode 6a is 522 cm^{-1} (517 cm^{-1}), 6b is 687 cm^{-1} (504 cm^{-1}), and 1 is 844 cm^{-1} (829 cm^{-1}) for dimethyl-*s*-tetrazine in *p*-xylene; and for phenyl-*s*-tetrazine in benzophenone the vibrational frequency of the ring breathing 6a is 328 cm^{-1} (325 cm^{-1}), 6b is 660 cm^{-1} (656 cm^{-1}), and 1 is 796 cm^{-1} (767 cm^{-1}). The vibrational intervals observed in the neat crystal spectra were comparable with the mixed crystal intervals. The radiative lifetime of the S_1 state was calculated from absorption data (in solution at 300 K) to be $(4.5 \pm 0.2) \times 10^{-7}$ s for dimethyl-s-tetrazine and $(4.8 \pm 0.2) \times 10^{-7}$ s for phenyl-*s*-tetrazine. The fluorescence lifetime of phenyl-*s*-tetrazine in benzene (300 K) is $(14.3 \pm 1.3) \times 10^{-9}$ s, corresponding to a fluorescence quantum yield of 0.03. Weak phosphorescence signals were detected from both dimethyl-*s*-tetrazine and phenyl-*s*-tetrazine following $S_1 \leftarrow S_0$ excitation at 1.6 K. The phosphorescence lifetime of the neat crystal at 1.6 K following direct triplet photoexcitation is $(85.2 \pm 3.4) \times 10^{-6}$ s for dimethyl-*s*-tetrazine and $(59.6 \pm 1.3) \times 10^{-6}$ s for phenyl-*s*-tetrazine corresponding to phosphorescence quantum yields of ca. 10^{-3}. The major depopulating mechanism of both the S_1 and T_1 excited states is predissociation. The reaction mechanism shows a marked spin selectivity $[k(S_1)/k(T_1) = 1.4 \times 10^4$ (dimethyl-*s*-tetrazine); 4.2×10^3 (phenyl-*s*-tetrazine)] and proceeds even in dilute mixed crystals at 1.6 K to produce directly the stable products $N_2 + 2CH_3CN$ from dimethyl-*s*-tetrazine and $N_2 + HCN + PhCN$ from phenyl-*s*-tetrazine without involving any intermediate species that was stable for an appreciable period of time.

I. Introduction

Recently some unique photochemical properties of *s*-tetrazine have been reported.[1-3] *s*-Tetrazine has consistently shown an apparent lack of intersystem crossing ($S_1 \rightsquigarrow T_1$) in the gas phase, in the condensed phase, and even in the low-temperature crystal. Although considerable speculation[4-6] has been given to the reported low quantum yields for fluorescence, phosphorescence, and triplet production, *s*-tetrazine has been shown to undergo photoinduced decomposition with near unit quantum yield in both gas[7] and condensed phase[1,2,8] to form the stable products N_2 and HCN.

To explore further the spectroscopy and photophysics of this interesting photochemical process dimethyl-*s*-tetrazine and phenyl-*s*-tetrazine were prepared. We report here the results of these studies. In particular, substitutional effects on the spectroscopy and the photophysical and photochemical behavior of the tetrazine chromophore have been studied at low temperatures.

Chowdhury and Goodman[9] reported the singlet–singlet absorption and emission of dimethyl-*s*-tetrazine at 300 K in the crystal and at 77 K in 3-methylpentane. The spectral origin was located at ca. 17150 cm^{-1} for both media. Hochstrasser and Marzzacco[10] identified the lowest triplet state of dimethyl-*s*-tetrazine at 13 113 cm^{-1} in absorption at 4.2 K in the crystal. They reported two vibrational intervals in the singlet–triplet spectrum. By comparison with the spectra of *s*-tetrazine and *p*-xylene they interpreted these intervals to correspond to the totally symmetric ring modes 6a′ (521 cm^{-1}) and 1′ (849 cm^{-1}). They also reported observing the 4.2 K crystal fluorescence (origin at ca. 17 100 cm^{-1}; 6a″ = 523 cm^{-1}; 1″ = 848 cm^{-1}), but were unable to detect any phosphorescence. de Vries and Wiersma[11] have recently reported the singlet–singlet absorption and fluorescence of dimethyl-*s*-tetrazine in durene at 2 K. They identified the spectral origin at 5875 Å and confirmed the upper state to be $^1B_{3u}$ (nπ*) by polarization measurements. Meyling, van der Werf, and Wiersma[8] reported the S_1 photochemical decomposition quantum yield to be 1.3 ± 0.3 and the fluorescence lifetime to be 6.0 ± 0.3 ns in the gas phase. In earlier work Strickler and Berg are reported to have determined the fluorescence lifetime[9] of dimethyl-*s*-tetrazine as 9.3 ns at 77 K and 4.1 ns at 300 K. Finally, there have been no spectroscopic or photochemical studies reported of phenyl-*s*-tetrazine.

II. Experimental Methods

2.1. Materials and Sample Preparation. Dimethyl-*s*-tetrazine was prepared by the method of W. Skorianetz and E. sz. Kováts[12] from the reaction of acetaldehyde and hydrazine [mp 67.5–68.5 °C (lit.