

cluded all configurations in the configuration interaction treatment and obtained the ordering of levels in Table V. It should of course be kept in mind that these are

Table V. SCF-CI Results on Oxyallyl<sup>a</sup>

<sup>1</sup> A <sub>1</sub>	4.136 <sup>b</sup>	<sup>1</sup> A <sub>1</sub>	0.112 <sup>b</sup>
<sup>1</sup> B <sub>1</sub>	1.967	<sup>3</sup> B <sub>1</sub>	[0.0]

<sup>a</sup> The states are labeled in C<sub>2v</sub> symmetry, with the xz plane being that of the molecule. <sup>b</sup> In electron volts.

$\pi$ -electron states only. In particular (n, $\pi^*$ ) excited states may arise at low energy in this molecule, but we have no reliable way to estimate their position. The <sup>1</sup>A<sub>1</sub> states are strong mixtures of the (S<sub>1</sub>)<sup>2</sup>(S<sub>2</sub>)<sup>2</sup> and (S<sub>1</sub>)<sup>2</sup>-

(A<sub>1</sub>)<sup>2</sup> configurations of Figure 21 while <sup>1</sup>B<sub>1</sub> and <sup>3</sup>B<sub>1</sub> represent predominantly the (S<sub>1</sub>)<sup>2</sup>(S<sub>2</sub>)<sup>1</sup>(A<sub>1</sub>)<sup>1</sup> configuration. <sup>3</sup>B<sub>1</sub> is the molecular ground state, but the singlet is not far above it in energy.

**Acknowledgment.** I am grateful to H. E. Simmons, R. J. Crawford, and R. B. Woodward for discussions concerning this work, and to A. Imamura, P. Clark, W. J. Hehre, and G. D. Zeiss for assistance with the calculations. The minimum searching methods used in exploring the approach of methylene to ethylene are due to K. D. Gibson. Motivation for a good part of this work was found in the interesting studies of R. C. Cookson. Generous support was provided by the Chevron Research Company, the Sloan Foundation, the National Institutes of Health, and the National Science Foundation.

## The Electronic Structure of Methylenes

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**Abstract:** LCAO MO calculations of the extended Hückel type are carried out on methylene and methyl-, dimethyl-, phenyl-, diphenyl-, vinyl-, formyl-, nitro-, cyclopropyl-, cyano-, dicyano-, fluoro-, difluoro-, chloro-, dichloro-, bromo-, dibromo-, trifluoromethyl-, and methoxymethylene. We have concentrated on the equilibrium geometries and distortions of the configurations which will give rise to the lowest singlet and triplet states of these molecules. Let us denote by  $\sigma$  the bent methylene in-plane orbital, by p the out-of-plane orbital. The configuration  $\sigma p$  from which will be derived the lowest triplet (and probable ground state) of these methylenes is bent for all molecules except the cyanomethylenes. The  $\sigma p$  minima are deep only for some of the halocarbenes and methoxymethylene. Where a  $\pi$ -electron system is attached to the carbene, the  $\sigma p$  configuration prefers to bend in-plane. Diphenylcarbene has a most complicated potential surface with the optimum  $\sigma p$  geometry for a bent and twisted C<sub>2</sub> molecule. The lowest singlet potential surfaces have more features still. With respect to in-plane bending there may arise one (formyl), two (alkyl, cyclopropyl), or three (vinyl, phenyl) minima and one of the three in the latter case may be a saddle point unstable with respect to out-of-plane bending. Or the molecule may prefer to bend out-of-plane (nitro). The features of these surfaces are predictable if one knows the relative energy of the two p orbitals of the "linear" geometry of the methylene. An analysis of the location of these levels in terms of the molecular orbitals of the substituents is presented.

In this paper we present the results of extended Hückel calculations on methylene and several of its substituted derivatives. Our object in making these calculation is to shed some light on the preferred conformation and electronic structure of the ground and first excited electronic configuration of these molecules.

It must be made clear at the outset that the extended Hückel calculations do not include electron interaction, and as such yield at best an estimate of the average energy of a configuration. They thus do not distinguish between a singlet and triplet state of a given spatial symmetry. In calculations on methylenes this is a particularly significant restriction and so we would like to elaborate on the electronic structure of methylenes, our notation, and precisely what we are and are not calculating.

For methylene itself, CH<sub>2</sub>, the ground state has been assigned by Herzberg<sup>1</sup> as <sup>3</sup> $\Sigma_g^-$ , linear or nearly linear (the corresponding bent symmetry designation is <sup>3</sup>B<sub>1</sub> in

C<sub>2v</sub>). At an undetermined but small energy above this state lies the lowest singlet, a C<sub>2v</sub>-<sup>1</sup>A<sub>1</sub> with an HCH angle of 102.4°. Some 2.0 eV above this lies a <sup>1</sup>B<sub>1</sub>, also bent, with HCH angle 140 ± 15°. Another 1.5 eV higher lies an unanalyzed <sup>1</sup>A<sub>1</sub> state. Theoretically it is clear that a linear methylene would have two perpendicular 2p orbitals ( $\pi_u$  in D<sub>∞h</sub>) into which two electrons are to be placed. This gives rise to three states, arranged in order of likely increasing energy as <sup>3</sup> $\Sigma_g^-$ , <sup>1</sup> $\Delta_g$ , <sup>1</sup> $\Sigma_g^+$ . On bending from D<sub>∞h</sub> to C<sub>2v</sub> geometry, one of the 2p orbitals, the one perpendicular to the plane in which the bending takes place, is to first order unaffected by the bending. This orbital transforms as b<sub>1</sub> in C<sub>2v</sub> and in the subsequent discussion will be referred to as simply "p." The other p orbital, a<sub>1</sub> in C<sub>2v</sub> symmetry, mixes with the corresponding symmetry 2s orbital on carbon (as well as with a 1s H combination and 1s on C). As a result of this mixing it is stabilized in energy ("it acquires s character"). We will refer to this

(1) G. Herzberg, *Proc. Roy. Soc., Ser. A*, **262**, 291 (1961).

(2) G. Herzberg and J. W. C. Johns, *ibid.*, **295**, 107 (1966).

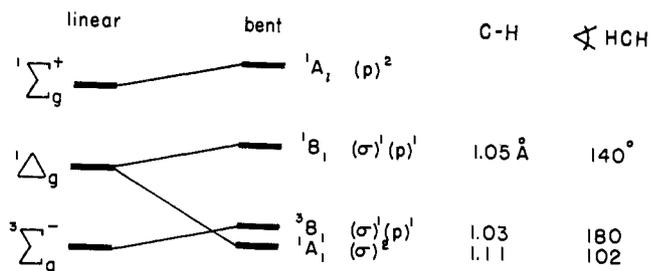


Figure 1. The known states of methylene, their molecular constants, and the electronic configurations from which they are derived. For uncertainties see ref 1 and 2.

$a_1$  orbital as " $\sigma$ " in the subsequent discussion. The ground configuration ( $\sigma$ )<sup>2</sup> gives rise to an  $1A_1$  state, whereas the excited configuration ( $\sigma$ )<sup>1</sup>( $p$ )<sup>1</sup> yields  $1B_1$  and  $3B_1$ , and the doubly excited ( $p$ )<sup>2</sup> gives rise to another  $1A_1$ . The terms "ground," "excited," and "doubly excited" are used above in the normal sense, *i.e.*, levels assumed occupied in order of increasing one-electron energy. In fact the difference in one-electron energy between  $\sigma$  and  $p$  is never very big over the range of HCH angles from 180 to 100°, at least as far as these energies are available from the best calculations.<sup>3</sup> The energy difference between  $\sigma$  and  $p$  is sufficiently small over this angle range that the more favorable electron interaction in the triplet  $B_1$  state stabilizes it to the extent that in fact it, formally arising from an excited electronic configuration, becomes the true ground state. The relationships among the various states and configurations of linear and bent  $CH_2$  are drawn in Figure 1. In substituted methylenes  $\sigma$  and  $p$  may be delocalized further but at least in our calculations they always remain clearly recognizable. Thus whereas their actual symmetry designations change with the pattern of substitution we will retain the  $\sigma, p$  nomenclature for describing configurations of substituted methylenes.

The extended Hückel calculations<sup>4</sup> do not include electron interaction, and thus can only give the average energy of a configuration, say ( $\sigma$ )<sup>1</sup>( $p$ )<sup>1</sup>. In the linear form they thus give the same energy for  $3\Sigma_g^-$ ,  $1\Delta_g$ , and  $1\Sigma_g^+$  and in the bent form give rise to only three energy curves, ( $\sigma$ )<sup>2</sup>, ( $\sigma$ )<sup>1</sup>( $p$ )<sup>1</sup>, ( $p$ )<sup>2</sup> (abbreviated below as  $\sigma^2$ ,  $\sigma p$ ,  $p^2$ ). Thus these calculations cannot possibly make an outright prediction as to what will be the ground state of the molecule. For methylene the calculations place the average energy of the  $\sigma p$  configuration above the  $\sigma^2$  for all angles. This is probably true in reality as well, but it does not allow any direct conclusion as to true ground-state symmetry. In practice we have sometimes used a rough empirical criterion for making a decision. This is the following: if the optimum  $\sigma^2$  configuration has an extended Hückel energy less than 1.5 eV below the  $\sigma p$  configuration at the same HCH angle then the ground state is likely to be in fact the triplet state derived from the  $\sigma p$  configuration.<sup>5</sup>

(3) (a) J. M. Foster and S. F. Boys, *Rev. Mod. Phys.*, **32**, 305 (1960).  
 (b) S. G. Peyerimhoff, R. J. Buenker, and L. C. Allen, *J. Chem. Phys.*, **45**, 734 (1966); L. C. Allen in "Quantum Theory of Atoms, Molecules and the Solid State," P. O. Löwdin, Ed., Academic Press Inc., New York, N. Y., 1966.

(4) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); **40**, 2474, 2480, 2745 (1964); *Tetrahedron*, **22**, 521, 539 (1966).

(5) It is difficult to give a theoretical justification of this criterion. It is based on our experience with extended Hückel calculations on benzenes and diradicals where the same problem arises. For methylenes it appears to work in the cases where information on the multi-

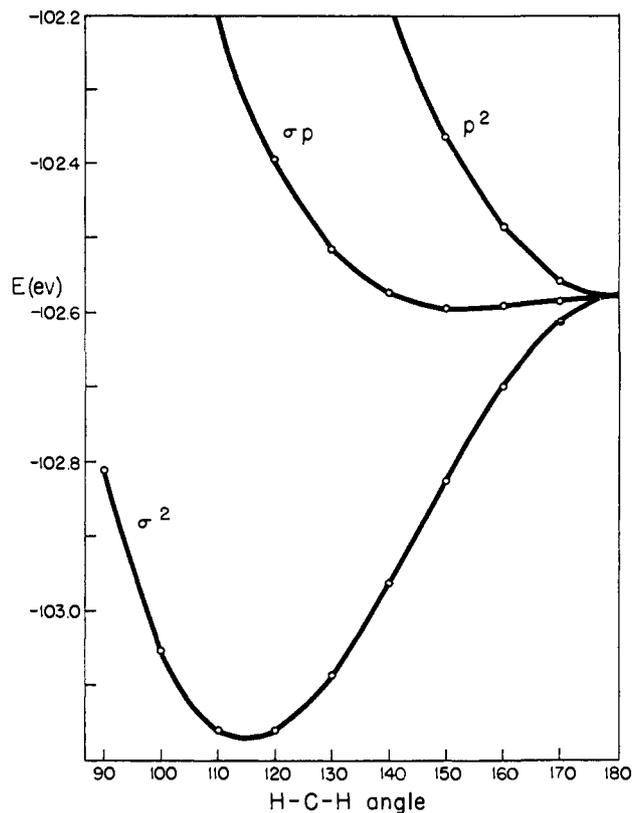


Figure 2. The energies of the lower  $CH_2$  configurations as a function of bending.

The real value of the calculations is that potential energy curves are generated for the average configurations. First we believe on the basis of our experience with these calculations that the correct angular dependence of the energy is reproduced by them. For the case of  $CH_2$  itself the opportunity for comparison with reality and good calculation is available to support this contention. Secondly we believe different spin states of the same spatial symmetry configuration possess approximately the same potential surfaces with respect to distortions near the equilibrium geometry. Again there is the opportunity to compare with experimental and theoretical conclusions for  $1B_1$  and  $3B_1$  of  $CH_2$ ;<sup>6</sup> there are some relevant cases in other molecules as well.<sup>7</sup> We thus believe that where configuration interaction is not great our calculated  $\sigma^2$  potential surface should be a good approximation to the  $1A_1$  potential surface and the  $\sigma p$  potential surface should serve as a faithful model of both the  $3B_1$  and  $1B_1$  surfaces. We estimate that the greatest source of error in our determination of the  $1A_1$  potential surface arises from the inability of our calculations to take into account the modification of this surface by configuration interaction. In many cases the CI mixing of the  $\sigma^2$  and  $p^2$  configurations must be strong and so the true lowest  $1A_1$  surface must become a hybrid of  $\sigma^2$  and  $p^2$  surfaces.

licity of the ground state is available. Thus it will be seen that in  $CF_2$  the splitting is greater than 1.5 eV and the molecule is known to be a singlet. In all other carbon-substituted carbenes the splitting is smaller than 1.5 eV and triplet ground states are implicated for most.

(6) See ref 3a and 3b.

(7) There are a great number of diatomic cases. See the tables in G. Herzberg "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules," D. Van Nostrand Co., Princeton, N. J., 1950. Few polyatomic cases are well analyzed, but one example is formaldehyde. See G. W. Robinson and V. E. DiGiorgio, *Can. J. Phys.*, **36**, 31 (1958).

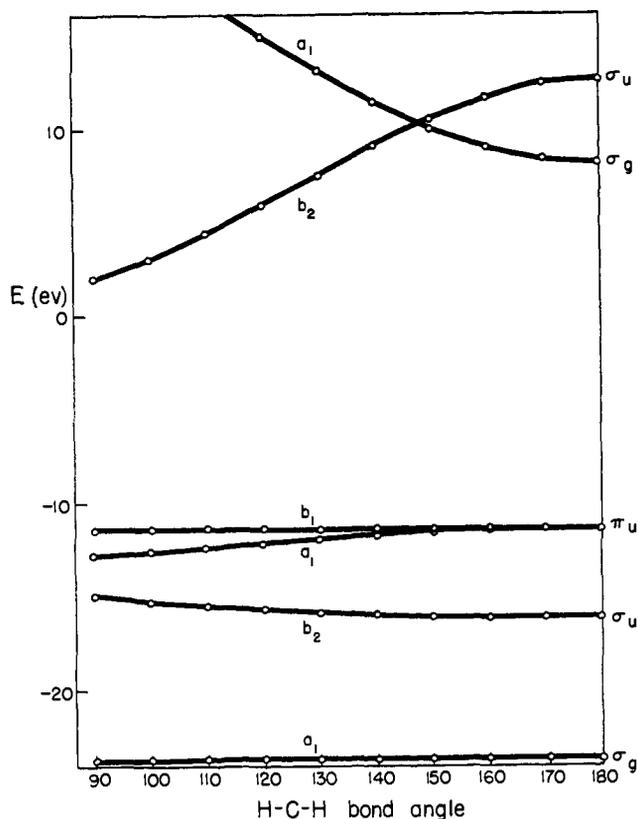


Figure 3. One-electron energy levels computed for  $\text{CH}_2$ .

### Methylene

Figure 2 shows our calculated potential energy curves for the  $\sigma^2$ ,  $\sigma p$ , and  $p^2$  configurations of methylene. A C-H distance of 1.10 Å was used consistently throughout these calculations. The  $\sigma^2$  configuration has a minimum at an HCH angle of approximately 115°, at an energy of 0.6 eV below the linear geometry.  $\sigma p$  has a very shallow minimum at an HCH angle of about 155°, at an energy only 0.013 eV below that of the linear form.  $p^2$  clearly prefers to be linear. The energy of  $\sigma^2$  at its minimum is not very far below that of optimum  $\sigma p$  so that one would anticipate that the ground state of the molecule is the triplet component of  $\sigma p$  configuration. The shape of the potential curves is in quite good agreement with the best available calculations. Thus both Foster and Boys<sup>3a</sup> as well as Allen and coworkers<sup>3b</sup> obtained slightly bent  $^3B_1$  methylenes with shallow minima, and considerably more bent  $^1A_1$  states. The potential curves for  $^3B_1$  and  $^1B_1$ , the two states derived from the  $\sigma p$  configuration, are strikingly parallel in the calculations of these authors, supporting our contention that the average energy of the configuration has an angular dependence very similar to that of the components. Figure 3 shows the variation of the one-electron energy levels as a function of bending. The diagram largely parallels a Walsh diagram for  $\text{XH}_2$ .<sup>8</sup> This is hardly surprising since the extended Hückel method can be viewed as a computer formalization of Walsh's method.

The analysis of the  $\text{CH}_2$  spectrum indicates a linear or near-linear  $\text{CH}_2$ .<sup>1</sup> It should be noted that in our calculations the position of the minimum in the  $\sigma p$  configuration is a sensitive function of the C-H distance used. At C-H = 1.00 Å (in fact closer to the experimental

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

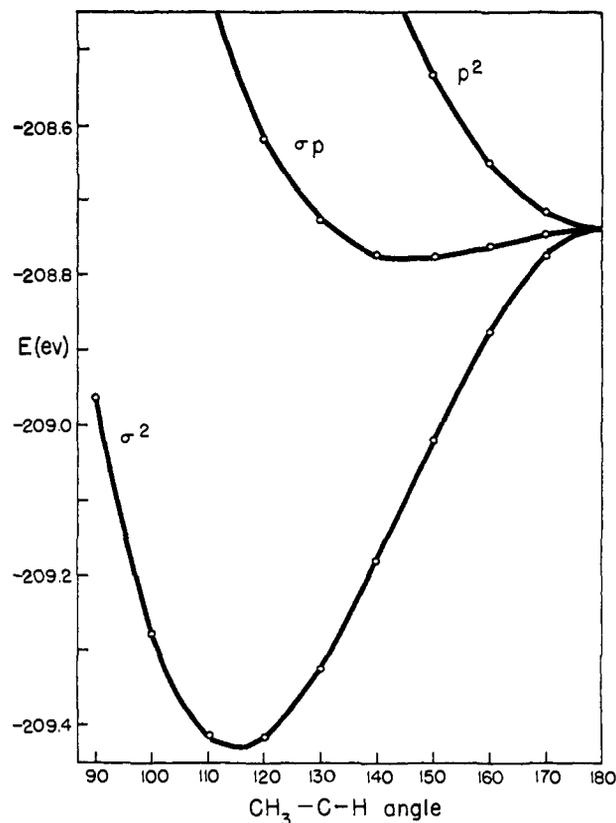


Figure 4. Configuration energies for methylenemethylene.

distance than the assumed 1.10 Å) the minimum is shallower still and occurs close to 175°.

### Methylenemethylene (Ethyldiene)

Figure 4 illustrates the potential energy curves for bending the C-H bond away from colinearity with the C- $\text{CH}_3$  bond. The C-C distance is taken as 1.54 Å. The methylene C-H is here maintained staggered with respect to the methyl group. The energy curves are very similar to those of  $\text{CH}_2$  itself, with minima for  $\sigma^2$  at 116°,  $\sigma p$  at 146.5°,  $p^2$  at 180°. If the same motion is studied for an ethyldiene in which the RC-H bond is eclipsing a C-H bond of the methyl group, very similar curves are obtained. In fact the curves are too close to be adequately represented on Figure 4, the  $\sigma^2$  configuration having a minimum at 117°, 0.027 eV above the staggered minimum, and the  $\sigma p$  configuration having a minimum at 147°, only 0.001 eV above the corresponding staggered minimum. The barrier to internal rotation is thus small in the  $\sigma^2$  configuration and negligible in  $\sigma p$ . The magnitudes are not to be trusted to better than a factor of two judging from our previous experience with these calculations, but it may be noted that the  $\sigma^2$  barrier is considerably smaller than that calculated for methanol. There is also very little deviation from an ideal threefold barrier, and the same is true for the much smaller  $\sigma p$  barrier.

Figure 5 shows an interesting detail of the ethyldiene calculations. This is the overlap population between the carbene carbon and one of the hydrogens of the adjacent methyl group, as a function of the rotation of that hydrogen from eclipsing the carbene C-H bond (0°) to being *trans* to it (180°). The reason for plotting these small variations is that they could be giving us a clue to

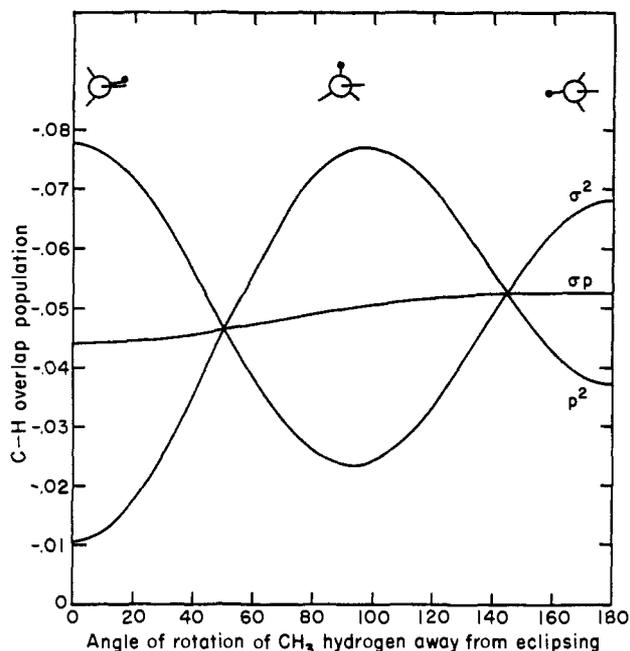
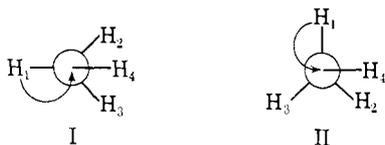


Figure 5. The overlap population between the methylene carbon and a methyl hydrogen for various states of  $\text{CH}_3\text{CH}$ . The CCH angle is  $120^\circ$  and the zero angle is at the  $\text{CH}_3$  hydrogen eclipsing the methylene hydrogen.

the preferred transition-state conformation in the ubiquitous rearrangement of ethylidene to ethylene. An interesting feature of this rearrangement to us is that if one imagines the hydrogen shifting over in such a way that least motion of it is involved, the *trans* initial conformation is indicated (I). But it is obvious that as such a transition state approaches ethylene the hydrogens are in an arrangement nearly as far as possible from a normal



planar ethylene. So perhaps another conformation such as II is favored. The rotational barriers in ethylidene are small, as we have seen, and while  $\text{H}_1$  has somewhat further to travel in II, the resulting ethylene is close to planar. The overlap populations between  $\text{H}_1$  and the carbene C vary only over a range of  $-0.08$  to  $-0.02$  but from our experience these small variations in nonbonded overlap populations often mirror incipient bonding changes. The trend in the  $\sigma^2$  configuration is as we anticipated above; the least negative overlap population is for an angle of  $90^\circ$ .  $p^2$  on the other hand has the largest overlap population for 0 and  $180^\circ$ , and the trend can be understood by a correlation with a nonplanar excited ethylene. We have begun to explore the ethylidene-ethylene potential surface in greater detail.

### Dimethylmethylene

Three conformations were studied in some detail. We define staggered (s) and eclipsed (e) configurations of the terminal methyl groups with respect to the C-other  $\text{CH}_3$  bond. The three conformations considered were then staggered-staggered (ss), staggered-eclipsed (se),

and eclipsed-eclipsed (ee). The shapes of the potential energy curves are not very different from the ethylidene case, and the positions and energies of the actual minima are summarized in Table I.

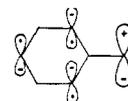
Table I

Conformation		Optimum CCC angle, deg	Energy, eV
$\sigma^2$	ee	$121.5 \pm 1$	-315.581
	se	121.0	-315.556
	ss	120.0	-315.547
$\sigma p$	ee	146.0	-314.903
	se	144.0	-314.906
	ss	143.0	-314.909

The behavior of the  $\sigma^2$  configurations near their minima is complex. The ee conformation has the lowest energy minimum but also rises most steeply at smaller angles. The latter observation as well as the general shift of the minima to greater CCC angles (compared to methylmethylene) are understandable. These effects are consistent with the consequences of the steric interference by the other methyl group, most acutely felt in the ee conformation. It remains difficult to rationalize that the lowest minimum of all is attained by the ee conformation of  $\sigma^2$ . If one thinks of  $\sigma^2$  as essentially possessing a lone pair on the divalent carbon, then the preferred staggered (with respect to H) conformation of methylmethylene seems to indicate that it is more advantageous to stagger H than the lone pair. In contrast the lowest energy ee conformation of dimethylmethylene seems to point to a preference for staggering the lone pair over a methyl group. The calculated barriers to internal rotation are obscured for  $\sigma^2$  by level reversal near the optimum angle; for  $\sigma p$  they remain very small at 0.003 eV.

### Phenylmethylene

In methylene itself as the geometry approached linearity the  $\sigma$  orbital approached a p orbital,  $p'$ , degenerate with p and perpendicular to it. In the lower symmetry of methyl- and dimethylmethylene, p was no longer strictly degenerate with  $p'$  in the linear configuration. The splitting was however miniscule, amounting to a maximum of 0.001 eV in dimethylmethylene. The situation is drastically different for phenylmethylene. Here in the linear geometry one of the p orbitals, called  $p_i$ , lies in the plane of the benzene ring. While interacting mildly with appropriate symmetry  $\sigma$  orbitals of the benzene ring, it is easily recognizable and distinctly localized. The other p orbital, called  $p_o$ , lies out of the benzene ring plane and interacts significantly with its  $\pi$  system. In fact the  $\pi$ -electron system of a phenylcarbene is extremely similar to that of benzyl, and what we have called  $p_o$  has the familiar shape of the nonbonding orbital of benzyl.



When the exocyclic C-C bond is taken as 1.54 Å, the extended Hückel calculations put  $p_o$  at  $-11.08$  eV,  $p_i$  at  $-10.90$  eV, an ordering which emerges as being crucial for the electronic structure of the molecule.

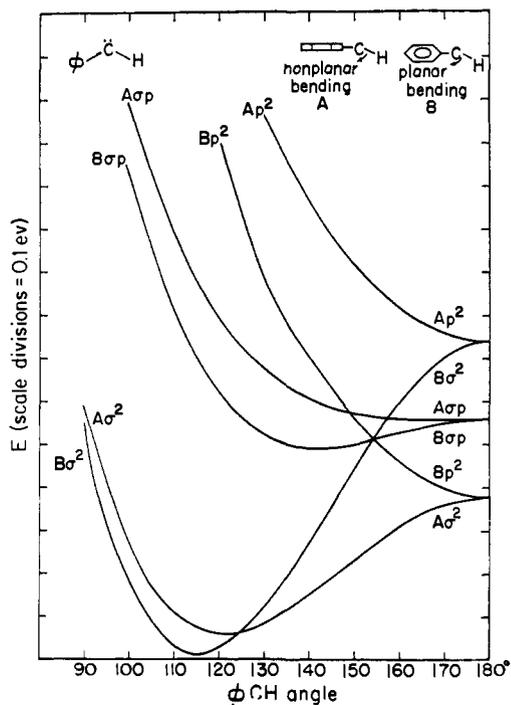
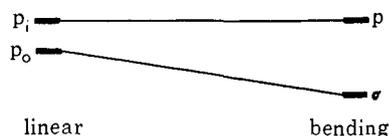


Figure 6. Configuration energies for phenylmethylene. A = out-of-plane bending, B = in-plane bending.

The two basic motions studied for phenylmethylene were in-plane and out-of-plane bending. We can anticipate the results of the detailed calculations by predicting the course of  $p_0$  and  $p_1$  under out-of-plane and in-plane bending.

(1) Out-of-plane bending:  $p_0$  is transformed into  $\sigma$ , acquires s character and is stabilized by the bending motion.  $p_1$  becomes p and is unaffected by the bending.



(2) In-plane bending:  $p_0$  is unaffected by the bending and now it becomes p.  $p_1$  acquires s character, and moves to lower energy with bending as it is transformed into  $\sigma$ .



A very interesting situation is thus created. For out-of-plane bending one expects a "normal" methylene type of potential energy curve, with a strongly bent  $\sigma^2$  configuration and a slightly bent  $\sigma p$ . For in-plane bending the lowest energy configuration for a linear form is  $p^2$ . The above diagrams would make one think at first that this configuration would not be much affected by bending, but in fact we know from the case of methylene itself that whereas the p level does not move in energy, the  $p^2$  configuration increases its energy sharply as bending is forced. The origin of this is in the upward slope of one of the lower occupied orbitals,  $b_2$  in symmetry. For phenylmethylene we would then expect the  $p^2$  configuration to increase in energy until it is

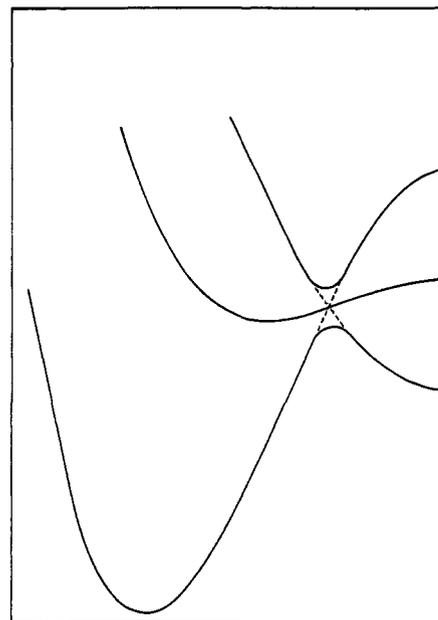


Figure 7. Schematic drawing of phenylmethylene states after electron interaction is included. The crossing of the two totally symmetric states is avoided.

crossed by the  $\sigma^2$  potential energy curve. The  $\sigma p$  minimum for in-plane bending should be deeper and at a smaller RCH angle than the corresponding out-of-plane minimum since for the former p originates from the stabilized  $p_0$ . This is precisely what happens, and the potential energy curves of the configurations are exhibited in Figure 6.

The crossing of the one-electron  $\sigma^2$  and  $p^2$  potential surfaces is avoided when electron interaction is taken into account. Allowing in-plane bending only the resulting potential curves will probably appear as indicated in Figure 7. The lowest singlet thus has three minima—two bent as well as a linear one. If one allows out-of-plane bending it becomes clear that the linear minimum is in fact a saddle point, stable with respect to in-plane bending but unstable with respect to out-of-plane motions. We have constructed a contour diagram of this fascinating potential surface in Figure 8. Clearly the way such a phenylmethylene would move from one in-plane minimum to another is through an out-of-plane rotation.

The  $\sigma p$  configuration, which will give rise to the triplet state that we would anticipate should be the ground state of the molecule, prefers an in-plane bent ( $\sim 143^\circ$ ) geometry by an energy that is still small (0.06 eV) but significantly greater than any of the other molecules we have examined here up to this point. One of the few experimental guideposts we have on the more complex substituted carbenes is available here. ESR studies of phenylmethylene in a glass matrix show the triplet to be nonlinear.<sup>9</sup> The estimate of the angle of bending from these experiments is only made possible through a theory of the dependence of zero-field splittings on bending.<sup>10</sup> The angle that is obtained in this way is  $\sim 155^\circ$ , but in our opinion the value is not very reliable.

The theoretical interpretation of the zero-field splittings of triplet-state methylenes is marked by some highly

(9) E. Wasserman, A. M. Trozzolo, W. A. Yager, and R. W. Murray, *J. Chem. Phys.*, **40**, 2408 (1964).

(10) J. Higuchi, *ibid.*, **38**, 1237 (1963); **39**, 1339 (1963).

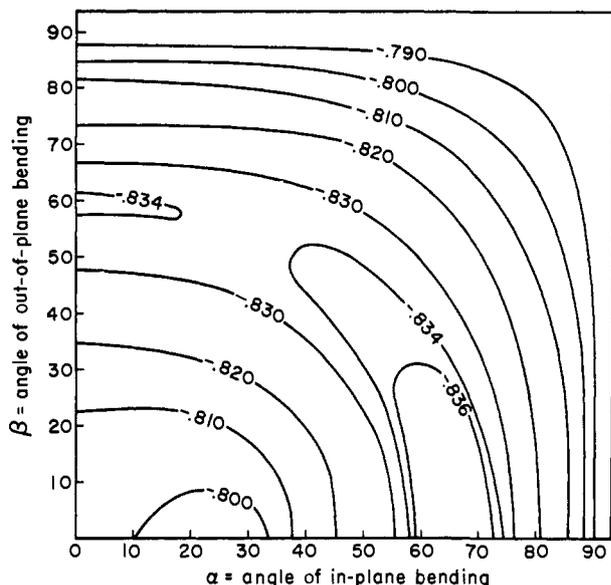


Figure 8. A contour diagram of the lowest energy configuration of phenylmethylene. A conformation is specified by bending in-plane through an angle  $\alpha$ , then bending down through an angle  $\beta$ . Thus for  $\beta = 0$  varying  $\alpha$  corresponds to in-plane bending only, and for  $\alpha = 0$   $\beta$  represents out-of-plane bending alone. The contours separate the figure space into equal areas.

sophisticated and interesting calculations and yet curiously marred by some uncritical assumptions about the composition of the  $\sigma$  orbital.<sup>9,10</sup> For instance the per cent *s* character (hybridization) is related to the bond angle by the usual hybridization formula. This leads to the situation (in fluorenylidene) that when the zero-field splitting parameters imply little *s* character that one is forced to construct some artificial argument about bent bonds.<sup>9</sup> Of course there is nothing in the structure of quantum mechanics which forces any *one* particular molecular orbital to obey preconceived notions about hybridization. Table II below shows for instance that our calculations (which may of course not be very near reality either) give very little *s* character in  $\sigma$  over a wide range of angles for phenylmethylene. Very similar numbers are obtained for diphenylmethylene.

Table II. Mulliken Gross Atomic Populations in 2*s* and 2*p* on C for the  $\sigma$  Orbital of Phenylmethylene Occupied by Two Electrons<sup>a</sup>

Angle, deg	2 <i>s</i> population	2 <i>p</i> population
180	0	1.824
160	0.010	1.784
140	0.033	1.684
120	0.056	1.552
100	0.072	1.408

<sup>a</sup> The difference between 2.00 and the sum of 2*s* and 2*p* is electronic density delocalized to the rest of the molecule.

### Diphenylmethylene

The three basic modes of bending are shown in Figure 9. In A and B the starting configuration is a planar  $D_{2h}$  diphenylmethylene, while in C it is a  $D_{2d}$  molecule with one phenyl group 90° out of the plane of the other. In B the bending maintains a planar  $C_{2v}$  molecule, while in A the bending is in a direction perpendicular to the

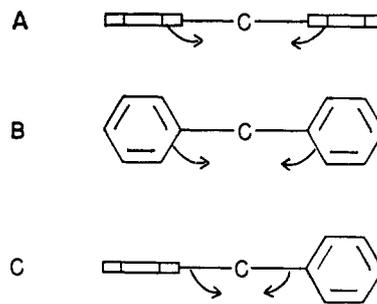


Figure 9. Three modes of bending for diphenylmethylene.

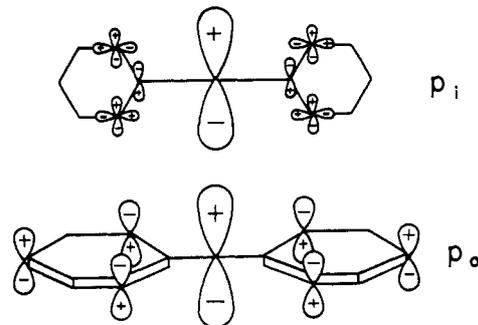


Figure 10. Composition of the out-of-plane ( $p_o$ ) and in-plane ( $p_i$ ) orbitals of a planar diphenylmethylene.

two phenyl rings. In the  $D_{2h}$  geometry, as in the phenylcarbene, the  $\pi$ -type  $p_o$  orbital is stabilized with respect to  $p_i$ . Both are shown in Figure 10.

We thus could anticipate the results of a comparison of A and B modes by utilizing the same argument as that used for phenylcarbene. That is, we expect for A a  $p^2$  configuration rising in energy with bending and intersecting a  $\sigma^2$  configuration which initially is at high energy but is progressively stabilized by the bending. In phenylmethylene the minimum of the planar bending (analogous to B) in fact came at a lower energy than that of the out-of-plane bending (like A). In diphenylmethylene this result would be difficult to predict since on top of these electronic considerations one must add on a pure steric effect. This would be expected to be most severe in mode B, where two *o*-hydrogens approach each other very early on in the bending.

The actual results are presented in the rather complicated Figure 11. The consequences of steric repulsion are apparent in every bending mode and are more severe than had been anticipated. First consider mode A, the out-of-plane bending. The  $A\sigma^2$  minimum is quite shallow and occurs at 134°, which is a larger angle for a  $\sigma^2$  configuration than any we have seen previously.  $A\sigma p$  and  $A p^2$  (not illustrated) both prefer the  $D_{2h}$  geometry. As expected the effect of crowding hydrogens is most apparent in the in-plane B mode of bending. This may be seen readily by focusing on the  $Bp^2$ ,  $B\sigma p$ , and  $B\sigma^2$  curves. The steric repulsion in fact sets in before  $\sigma^2$  and  $p^2$  cross (at ~138°); it damages so severely the intention of  $B\sigma^2$  to move to lower energy that for diphenylmethylene the lowest singlet should clearly be a mode A, out-of-plane bent molecule.

In the starting conformation of the C mode  $p_o$  and  $p_i$  are degenerate, transforming as *e* in  $D_{2d}$  symmetry. They can be written down as benzylic in one of the rings. The "linear" configuration of C comes in energy between  $p_o^2$  and  $p_i p_o$  of A and B.  $C\sigma^2$  also feels the ef-

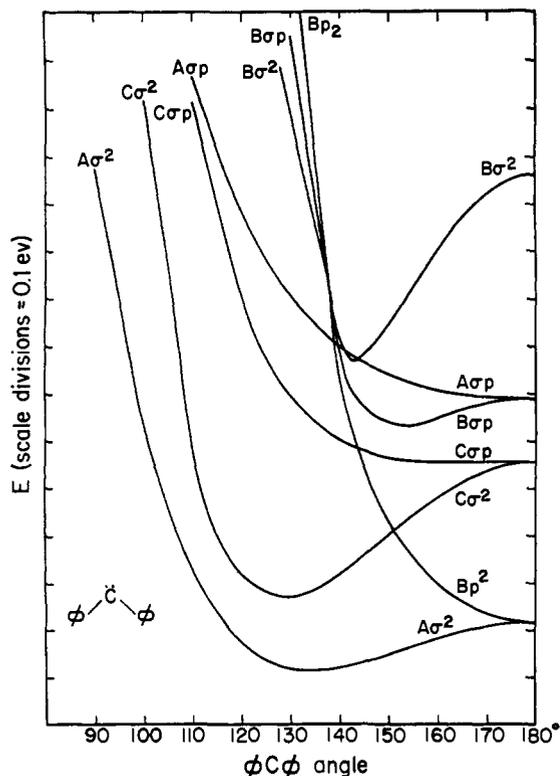


Figure 11. Computed configuration energies for some of the lower states of diphenylmethylene. A, B, and C modes are defined in Figure 9.

fects of steric crowding, and the minimum it attains at  $130^\circ$  is above the  $A\sigma^2$  minimum.

The  $\sigma p$  configurations, from which will arise the true ground state of the molecule, also present a complicated picture. Figure 11 shows the  $A\sigma p$ ,  $B\sigma p$ , and  $C\sigma p$  potential energy curves. In a linear geometry the two phenyl rings clearly prefer to be perpendicular. The  $C\sigma p$  curve has a shallow minimum at about  $170^\circ$ , whereas  $B\sigma p$  (in-plane bending) has a deeper minimum at  $154^\circ$ , and  $C\sigma p$  (out-of-plane bending) has a minimum for a linear conformation.

But these extremes of geometry do not in fact contain the minimum energy point of the  $\sigma p$  configuration. The fact that  $B\sigma p$  has a clear minimum but the disadvantage of starting out at  $180^\circ$  in a planar configuration makes it worthwhile to search the configuration space between conformations A, B, and C as a function of bending. After some initial exploration (at 3 min a point) we constructed the most favorable potential surface. To construct a geometry in this surface we applied sequentially two rotations,  $\theta$  and  $\psi$ , to a planar and "linear" diphenylmethylene. These are shown in Figure 12. First we bent the  $\phi C\phi$  angle from  $180^\circ$  to an angle  $\theta$ . Then we rotated both phenyl rings around their respective C- $\phi$  axes by the same angle  $\psi$ , in such a way that the resulting molecule possessed a twofold symmetry axis. A rough potential surface is shown in Figure 13. The lowest point on it is for  $\theta \sim 165^\circ$  and  $\psi \sim 45^\circ$ , i.e., a bent and twisted molecule of  $C_2$  symmetry. The energy magnitudes involved in these motions are very small, and the inclusion of electron interaction could easily modify the shape of the surface. We do feel, however, that the lowest triplet (and ground state) of diphenylcarbene will be both twisted and bent

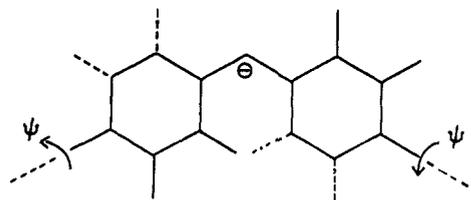


Figure 12. The preferred conformation for  $\sigma p$  diphenylmethylene and the definition of rotation variables for Figure 13. See text.

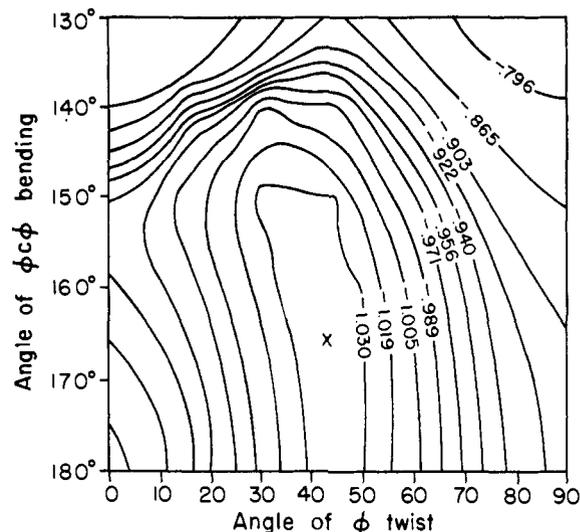


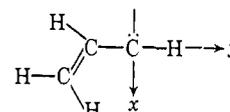
Figure 13. A contour diagram of  $\sigma p$  diphenylmethylene. Angle of  $\phi C\phi$  bending corresponds to  $\theta$  of Figure 12, angle of  $\phi$  twist to  $\psi$ .

from a  $D_{2d}$  geometry. The experimental results are not in disagreement with this conclusion.<sup>11,12</sup>

It should also be noted that the  $\sigma^2$  and  $\sigma p$  minima in this molecule are closer in one-electron energy than in any of the previous molecules. This should lead to a triplet-singlet gap larger than usual. This further result of steric hindrance has been anticipated elsewhere.<sup>13</sup>

### Vinylmethylene

The molecule was located in the  $xy$  plane. The bond lengths used were  $C=C$  1.34,  $C-C$  1.54,  $C-H$  1.07 Å;



all CCC angles were  $120^\circ$ . "In-plane" bending took place in the  $xy$  plane, "out-of-plane" in the  $yz$  plane.

As with phenylmethylene we can begin by considering the p orbitals of the methylene carbon in the "linear" geometry (CCH angle  $180^\circ$ ). Again  $p_1$  is the orbital in the plane of the molecule and is unchanged by moving the C-H bond in the  $yz$  plane (i.e., out-of-plane bending). Similarly  $p_0$  is unchanged by in-plane bending, but  $p_1$  (which becomes  $\sigma$ ) is stabilized and eventually goes below  $p_0$ . Thus the diagrams in the section on phenyl-

(11) R. W. Murray, A. M. Trozzolo, E. Wasserman, and W. A. Yager, *J. Amer. Chem. Soc.*, **84**, 3213 (1962); A. M. Trozzolo, R. W. Murray, and E. Wasserman, *ibid.*, **84**, 4990 (1962).

(12) C. A. Hutchison, Jr., *J. Phys. Chem.*, **71**, 203 (1967); R. W. Brandon, G. L. Closs and C. A. Hutchison, Jr., *J. Chem. Phys.*, **37**, 1878 (1962); R. W. Brandon, G. L. Closs, C. E. Davoust, C. A. Hutchison, Jr., B. E. Kohler and R. Silbey, *ibid.*, **43**, 2006 (1965).

(13) H. E. Zimmerman and D. H. Paskovich, *J. Amer. Chem. Soc.*, **86**, 2149 (1964).

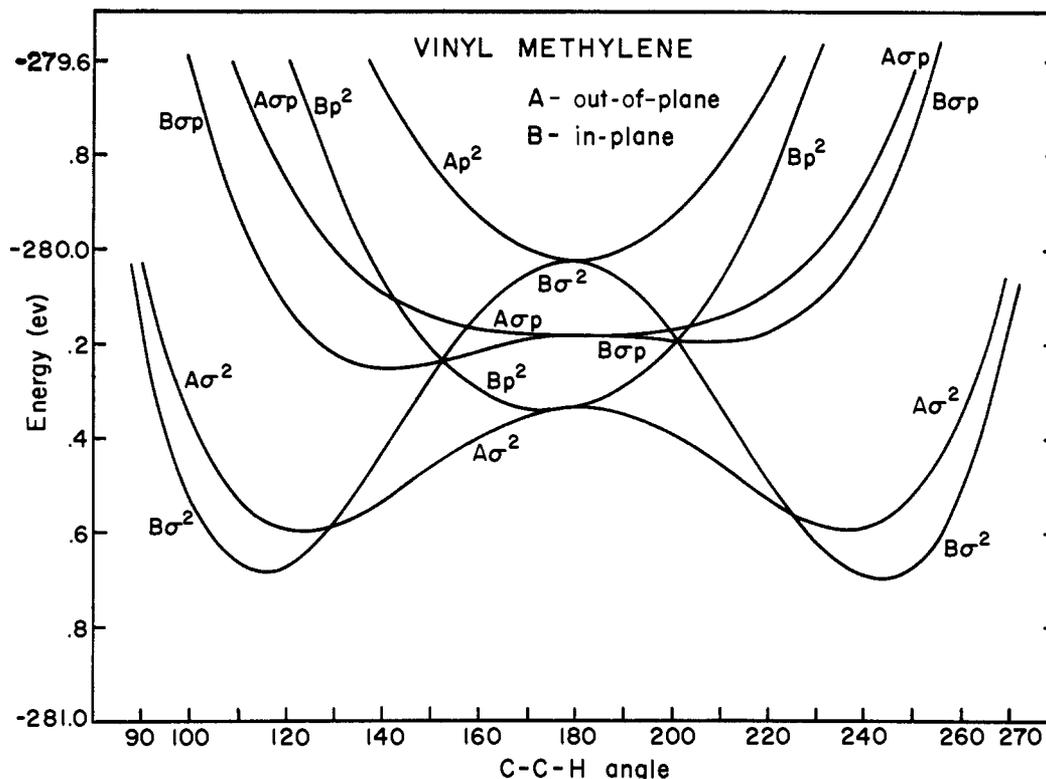


Figure 14. Configuration energies for vinylmethylene.

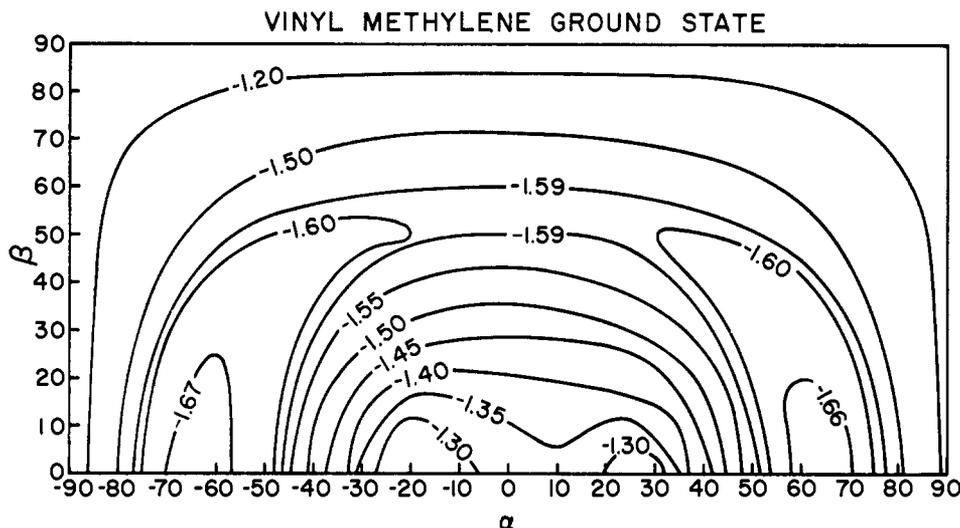


Figure 15. Contour diagram for lowest energy configuration of vinylmethylene. See text for definition of  $\alpha$  and  $\beta$ .

methylene are applicable here as well. In the "linear" geometry  $p_0$  is at  $-11.16$  eV,  $p_1$  at  $-11.00$  eV.

The computed potential energy curves for in- and out-of-plane bending are drawn in Figure 14. The resemblance to the phenylmethylene results (Figure 6) is remarkable. The natural distinction is that in vinylmethylene the in-plane bending curves are slightly unsymmetrical. The lowest singlet should be an in-plane bent molecule; the *cis* and *trans* conformations are of very nearly equal stability. The lowest triplet, and very likely ground state of vinylmethylene, will arise from the  $\sigma p$  configuration. This, in our calculations, has a shallow minimum at  $140^\circ$  in-plane bending. This minimum is pronounced only on the *cis* side (carbene H

relative to vinyl group) and the curve is nearly flat over a wide range of angles on the *trans* side.

Figure 15 is a contour diagram of the lowest energy configuration of vinylcarbene. The general motion of the methylene H is described by two angles,  $\alpha$  and  $\beta$ . Starting from the "linear" geometry we bend in plane by an angle  $\alpha$ . Positive  $\alpha$  implies bending in the  $+x$  direction, *i.e.*, toward *cis* geometry. After the in-plane bending is carried out we move the hydrogen downward toward the  $z$  axis by an angle  $\beta$ . In this way for a given C-H bond distance, all intermediate points between "in-plane" and "out-of-plane" bending can be calculated. Thus in Figure 15, a horizontal motion along the  $\beta = 0^\circ$  line corresponds to "in-plane" bending, and

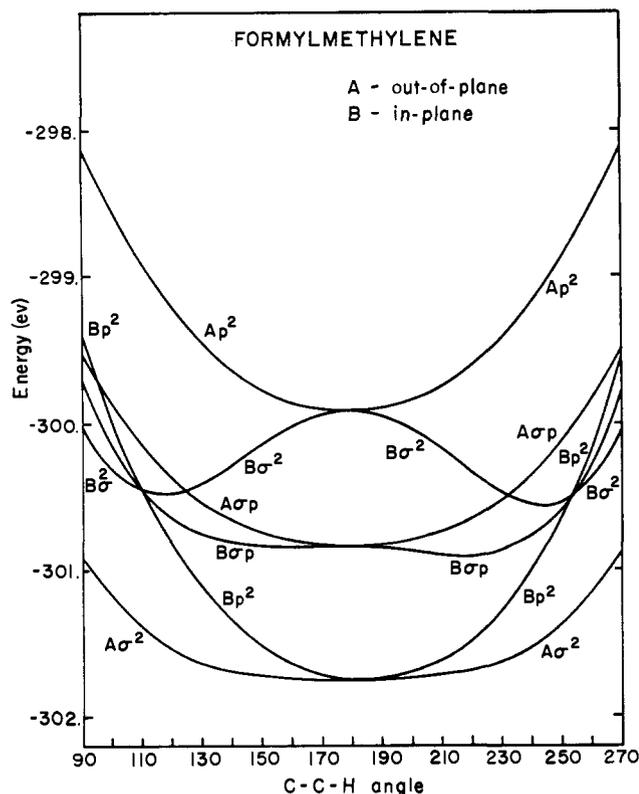


Figure 16. Configuration energies for formylmethylenes.

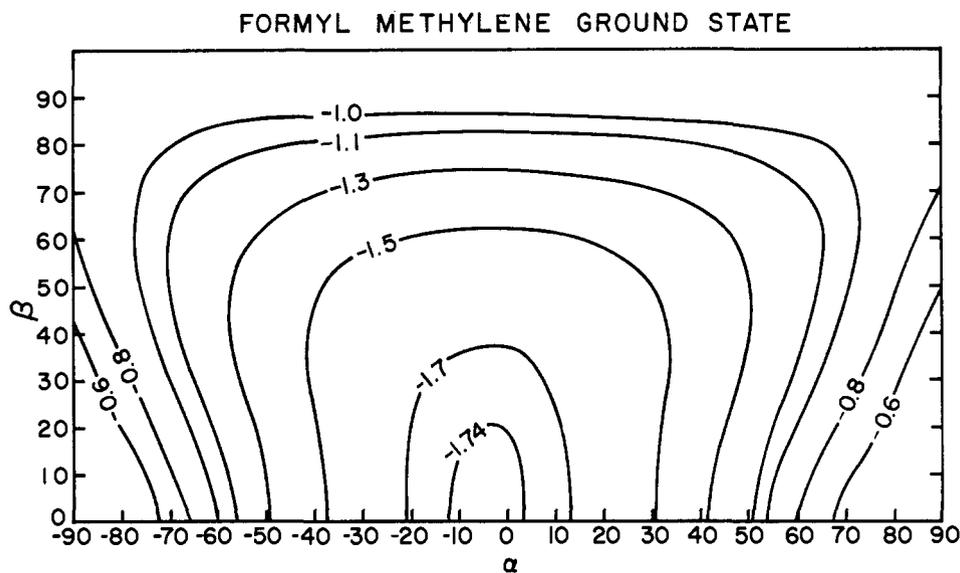


Figure 17. Contour diagram for the lowest energy configuration of formylmethylenes.

a vertical motion along the  $\alpha = 0^\circ$  line corresponds to “out-of-plane” bending.

It is noted from Figure 15 that the ground-state singlet minimum energy geometry is exactly the minimum in the “in-plane” bending curve,  $\alpha = \pm 62^\circ$ , bond angle =  $118, 242^\circ$ . The shallow minimum in the nearly linear geometry ( $\alpha = 5-10^\circ$ ) is seen, however, to be a saddle point—a *minimum* with respect to in-plane bending but a *maximum* with respect to out-of-plane bending (*i.e.*, along the line  $\alpha = 5^\circ, \beta = 0-90^\circ$ ).

This diagram also shows that the minimum energy path between the two bent minima ( $\pm 62^\circ$ ) is the out-of-

plane path, that is, motion in a semicircle around the contour diagram rather than horizontally along the  $\beta = 0^\circ$  line.

In phenyl- and vinylmethylenes the presence of the adjacent  $\pi$ -electron system stabilized the  $p_o$  orbital in the “linear” geometry with a resultant potential surface for the lowest singlet containing three minima for in-plane bending. We then thought of designing an extreme situation in which  $p_o$  would be stabilized further, perhaps to the point where there would be only a single linear  $p^2$  minimum for in-plane bending.

One way to accomplish stabilization of  $p_o$  is to attach a  $\pi$ -electron system with a low-lying unfilled  $\pi^*$  orbital, *i.e.*, a good electron acceptor. With this aim in mind, we have tried formyl, nitro, and cyclopropyl substituents.

#### Formylmethylenes

The orientation of this molecule was chosen to correspond as closely as possible to that used for vinylmethylenes. The definitions of in- and out-of-plane bending and  $\alpha$  and  $\beta$  thus remain as in the previous section. We used the following parameters: distances C—C 1.54, C=O 1.24, C—H 1.10 Å; all angles except at methylene carbon  $120^\circ$ ; oxygen Slater exponent of 2.275,  $H_{ii}(2s) - 32.30$  eV,  $H_{ii}(2p) - 14.80$  eV.

Our anticipation of stabilization of  $p_o$  was confirmed. In the “linear” geometry  $p_o$  was at  $-12.13$  whereas  $p_i$  was at  $-11.21$  eV. A consequence of this stabilization is that for CCH angles between  $110$  and  $255^\circ$ , the  $p$

orbital remains below  $\sigma$ . This is to be compared with vinylmethylenes where  $p$  was below  $\sigma$  over the narrower range between  $153$  and  $200^\circ$ . Figure 16 shows the energy curves as a function of in-plane and out-of-plane bending. As a result of the stabilization of  $p_o$  the intersection of  $B\sigma^2$  and  $Bp^2$  curves takes place only at a CCH angle where the  $B\sigma^2$  energy is *rising* again. Thus for in-plane bending there are here not *three* minima (as for phenyl or vinyl) but only *one*. Moreover this single, nearly linear, minimum is now not a saddle point (as was the linear well in phenyl or vinyl) but is a true minimum, stable with respect to out-of-plane bending.

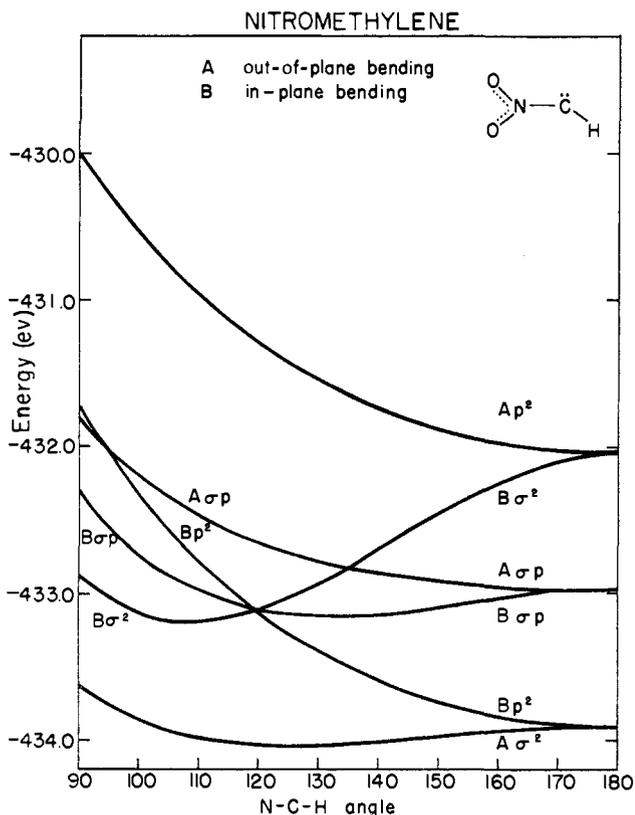


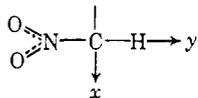
Figure 18. Configuration energies for nitromethylene.

This is illustrated clearly in Figure 17, a contour diagram for combined bending.

The  $\sigma p$  configuration prefers an in-plane *trans*-bent geometry. The energy difference between ground and excited configurations here is quite large, approaching a possibility of a singlet ground state. Experimental information on formylmethylene is lacking. It appears to have been recently prepared as an intermediate in the copper-catalyzed decomposition of diazoacetaldehyde. In the presence of an olefin the expected cyclopropane-carboxaldehyde is produced.<sup>14</sup> We hope to do some calculations in the future on the transition state for a rearrangement of formylmethylene to ketene.

### Nitromethylene

The molecule is oriented as below with the nitro group in the  $xy$  plane. The parameters used were: distances



C-N 1.49, N-O 1.22, C-H 1.10 Å; angle ONO 127°; nitrogen Slater exponent 1.950,  $H_{1s}(2s) -26.00$ ,  $H_{1s}(2p) -13.40$  eV. The definitions of in- and out-of-plane bending,  $\alpha$  and  $\beta$ , remain the same as in vinyl- and formylcarbene.

As expected the  $p_o$  level is stabilized. It appears at  $-12.09$  eV in the "linear" (H along  $y$  axis) geometry, whereas  $p_i$  remains at  $-11.15$ . The general results exhibited in Figure 18 are intermediate between vinyl and phenyl on one hand, and formyl on the other. As a result of the stabilization of  $p_o$  the in-plane bent  $B\sigma^2$  con-

(14) Z. Arnold, *Chem. Commun.*, 299 (1967).

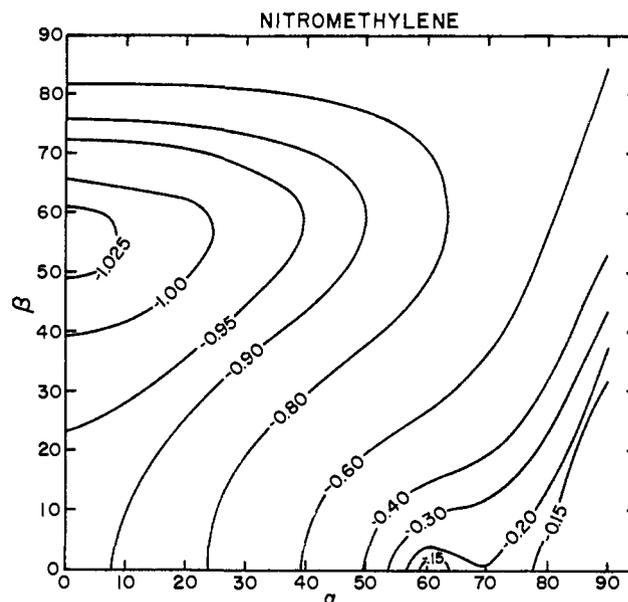


Figure 19. Contour diagram for the lowest energy configuration of nitromethylene.

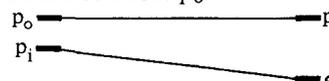
figuration never is quite at low enough energy to come below  $A\sigma^2$ . There are three minima with respect to in-plane bending, but the outer ones are shallower than the middle one, and that one is once again a saddle point, unstable with respect to out-of-plane bending leading to a very shallow minimum. These features are clearly displayed in the contour diagram (Figure 19). The lowest singlet of nitrocarbene should thus be bent out of plane, *i.e.*, to a  $C_s$  geometry. The lowest triplet should be bent in plane.

### Cyclopropylmethylene

The molecule is oriented as in Figure 20. The origin is at the carbene carbon, plane 1 is the  $xy$  plane, plane 2 the  $yz$  plane. Plane 1 bisects the cyclopropane ring and we will refer to bending in this plane as "in plane," whereas bending in the  $yz$  plane we will term "out of plane." This definition is consistent with our previous analysis of  $\pi$ -electron systems next to a carbene since the  $\pi$ -like Walsh orbital of the tertiary cyclopropane carbon lies in the  $yz$  plane.

The first sign of the unusual character of cyclopropylmethylene was the ordering of levels in the linear geometry. We found  $p_i$  at  $-11.01$ ,  $p_o$  at  $-10.72$ . There was no reason to expect stabilization of  $p_o$ , since there are no very low-lying unfilled orbitals in the cyclopropane, but the destabilization was unexpected. Among the carbon-substituted methylenes we have studied, cyclopropylcarbene has the highest energy  $p_o$ . We will return in a separate section at the end of this paper to an explanation of this result, but for the moment let us look at its consequences.

Since  $p_i$  is now below  $p_o$  the behavior of the two levels with bending is now reversed from that which we first described for phenylcarbene. In-plane bending stabilizes  $p_i$  but does not affect  $p_o$ .



but out-of-plane bending stabilizes  $p_o$  and creates a crossing.

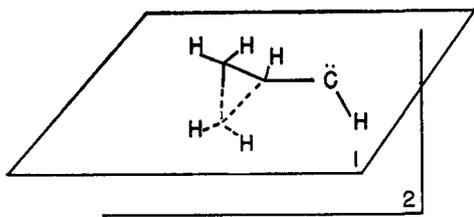


Figure 20. The orientation of a cyclopropylmethylene. The origin is at the carbene carbon; plane 1 is the  $xy$  plane, plane 2 is the  $yz$  plane; the intersection of the planes is thus the  $y$  axis.

The result is a set of potential curves (Figure 21) unlike any we have obtained before. The lowest singlet



will be a clearly in-plane bent molecule, with two normal minima. The lowest triplet and very probable ground state prefers to be in plane bent, with a now typical shallow minimum.

There is a further complexity and attendant inaccuracy in Figure 21. In the out-of-plane bending diagram sketched above,  $p_0$  and  $p_1$  intend to cross but are in fact prevented from doing so as a result of the lack of any symmetry in the out-of-plane bent geometry. The avoided crossing of  $A\sigma^2$  and  $Ap^2$  configurations would be invisible on the scale of Figure 21, and we show the region near  $145^\circ$  greatly enlarged in Figure 22. The crossing is of necessity avoided but only barely so. As is usual in avoided crossings the levels which are prevented from crossing take on very quickly the character or composition they would have had had they crossed. It is for this reason that we have labeled the lowest  $A$  mode curve as  $A\sigma^2$  at angles greater than  $215^\circ$  and less than  $145^\circ$ , even though it is formally connected to what started out to be an  $Ap^2$  curve.

### Cyanomethylene, Dicyanomethylene, and Propargylene

We used bond lengths of  $C-C$  1.54,  $C\equiv N$  1.15 Å in the cyanomethylenes. The total energy curves for these molecules are uncomplicated, and are shown in Figure 23. The  $\sigma p$  configuration in this case prefers a linear geometry. The  $\sigma^2$  minima are shallow and at large angles. Dicyanomethylene yields the flattest  $\sigma^2$  curve we have seen in these calculations. There is no doubt that the ground state of these molecules will be a linear triplet.

The potential energy surface for bending propargylene from an initial geometry with an assumed  $C_1-C_2$  1.21,  $C_2-C_3$  1.46 Å is also shown in Figure 23. The  $\sigma^2$  minimum is somewhat shallower and at a wider  $HCC_2H$  angle than previous molecules, and the  $\sigma p$  state clearly prefers a linear geometry. Experimentally the lowest triplet state of the molecule is linear.<sup>15</sup>

We have found the extended Hückel calculations unreliable for bond length calculations, and an attempt to determine if the  $\sigma p$  configuration preferred equal or unequal CC bond lengths led to absurd results. We intend to try some SCF calculations addressed to this problem.

(15) R. A. Bernheim, R. J. Kempf, J. V. Gramas, and P. S. Skell, *J. Chem. Phys.*, **43**, 196 (1965); P. S. Skell and J. Klebe, *J. Amer. Chem. Soc.*, **82**, 247 (1960).

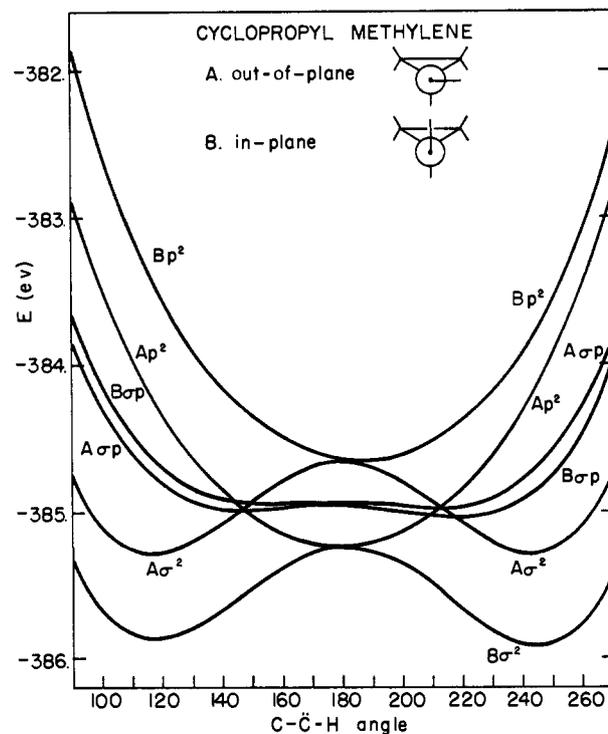


Figure 21. Configuration energies for cyclopropylmethylene. The  $A\sigma^2$  and  $Ap^2$  curves do not actually cross (see text) but they are labeled as if they had crossed.

### Halomethylenes

We have also carried out some calculations on  $CF_2$ ,  $CCl_2$ ,  $CBr_2$ ,  $CHF$ ,  $CHCl$ , and  $CHBr$ . We consider these somewhat less reliable than the previous calculations for two reasons. First we have had little experience with F and virtually none with Cl and Br within the framework of extended Hückel calculations. Any agreement with experimental results could be a coincidence as a result of the many parameters available. Secondly in the case of F there is a good deal of evidence that extended Hückel calculations are particularly unreliable as a result of the high polarity of the bonds. Figure 24 presents the calculated potential energy curves for  $CX_2$ , and for  $CHX$  molecules. The parameters of the calculations are listed below. The Slater exponents are due to Clementi<sup>16</sup> (see Table III).

Table III

	F	Cl	Br
$ns$ exponent	2.564	2.356	2.638
$np$ exponent	2.550	2.039	2.257
$H_{ii}(2s)$	-40.0	-30.0	-28.0
$H_{ii}(2p)$	-18.1	-15.0	-14.0
C-X distance	1.33	1.72	1.89

In Table IV we list the equilibrium angles for the  $\sigma^2$  and  $\sigma p$  configurations of these molecules, the depth of the  $\sigma p$  minima, and the energy difference between the equilibrium  $\sigma^2$  and  $\sigma p$  configurations.

In the series  $CF_2$ ,  $CCl_2$ ,  $CBr_2$ , and  $CH_2$  there is a steady increase in the equilibrium  $XCX$  angle for both  $\sigma^2$  and  $\sigma p$

(16) E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963).

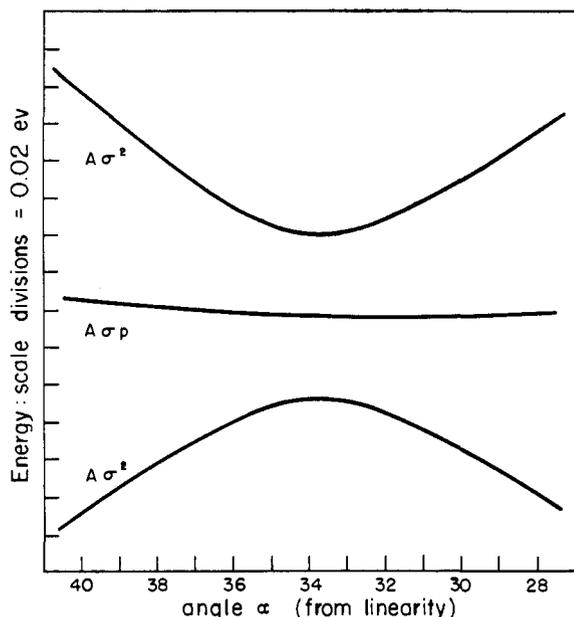


Figure 22. An enlarged view of the avoided crossing of  $A\sigma^2$ ,  $A\sigma p$ , and  $A\sigma^2$ .

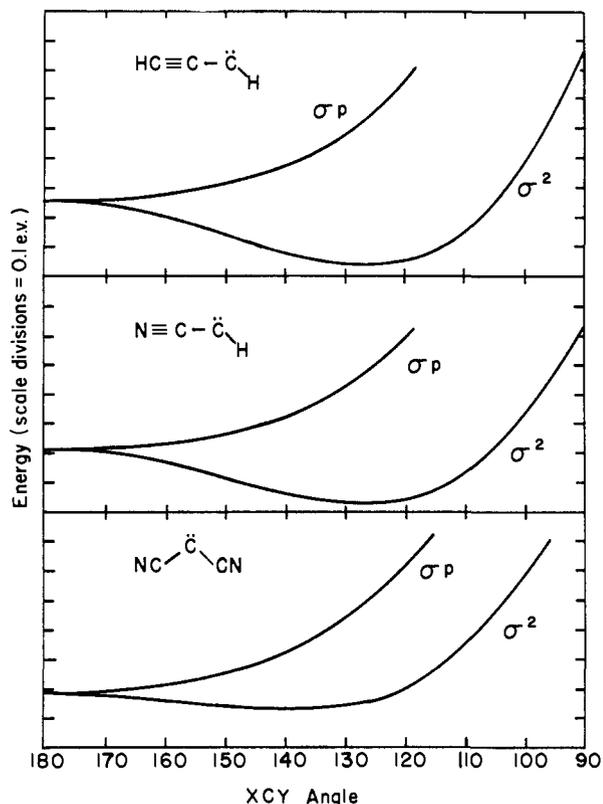


Figure 23. Configuration energies for cyanomethylene, dicyanomethylene, and propargylene.

configurations. There is a corresponding decrease in the depth of the  $\sigma p$  minimum and the energy difference between optimum  $\sigma p$  and  $\sigma^2$  geometries. The effect is particularly dramatic in  $\text{CF}_2$  which should clearly be a ground-state singlet, and in fact is such.<sup>17</sup> It is difficult to predict anything about the true ground states of  $\text{CCl}_2$  and  $\text{CBr}_2$  because whereas the  $\sigma p - \sigma^2$  difference is

(17) J. Duchesne and L. Burnelle, *J. Phys. Chem.*, **21**, 2005 (1953); C. W. Mathews, *ibid.*, **45**, 1068 (1966), and references therein.

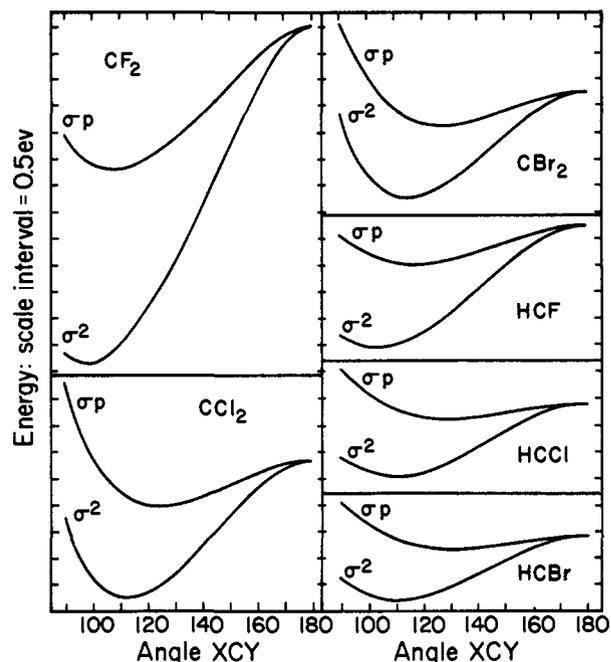


Figure 24. Energies of  $\sigma^2$  and  $\sigma p$  configurations for  $\text{CF}_2$ ,  $\text{CCl}_2$ ,  $\text{CBr}_2$ ,  $\text{HCF}$ ,  $\text{HCCl}$ , and  $\text{HCBBr}$ . The energy scale is the same for all drawings.

decreasing, one would also expect the singlet-triplet splitting of the  $\sigma p$  configuration to decrease. A fine discussion of the halocarbenes has been given by Simons.<sup>18</sup>

Table IV. The Halomethylenes

Molecule	Angle of minimum, deg $\sigma^2$	Angle of minimum, deg $\sigma p$	Depth of $\sigma p$ minimum, eV	$E(\sigma p) - E(\sigma^2)$ , eV
$\text{CF}_2$	$98 \pm 1$	$108 \pm 1$	3.0	3.6
$\text{CCl}_2$	112	124	0.8	1.8
$\text{CBr}_2$	114	126	0.6	1.4
$\text{CH}_2$	115	155	0.0	0.6
$\text{CHF}$	103	116	0.7	1.6
$\text{HCl}$	110	129	0.3	1.1
$\text{CHBr}$	111	131	0.2	1.0

The mixed hydrohalomethylenes  $\text{HCX}$  show behavior intermediate between that of  $\text{CH}_2$  and  $\text{CX}_2$ . The long-wavelength transitions of  $\text{HCF}$  and  $\text{HCCl}$  have recently been analyzed.<sup>19</sup> Both molecules possess singlet ground states with equilibrium angles of approximately  $103^\circ$  for  $\text{HCl}$  and  $102^\circ$  for  $\text{HCF}$ . The upper states are  $^1A'$ , derived from the  $\sigma p$  configuration, with angles of  $135^\circ$  for  $\text{HCCl}$  and  $127^\circ$  for  $\text{HCF}$ . These angles are in the order calculated in Table II, but quantitative agreement is not good. The depth of the  $\sigma p$  minimum does correlate well with the experimental estimates.

Why does  $\text{CF}_2$  have so much deeper minima for  $\sigma^2$  and  $\sigma p$  states than  $\text{CH}_2$ ? We can trace the answer clearly back one stage and less clearly beyond. The

(18) J. P. Simons, *Nature*, **208**, 1308 (1965).

(19) A. J. Merer and D. N. Travis, *Can. J. Phys.*, **44**, 525, 1541 (1966).

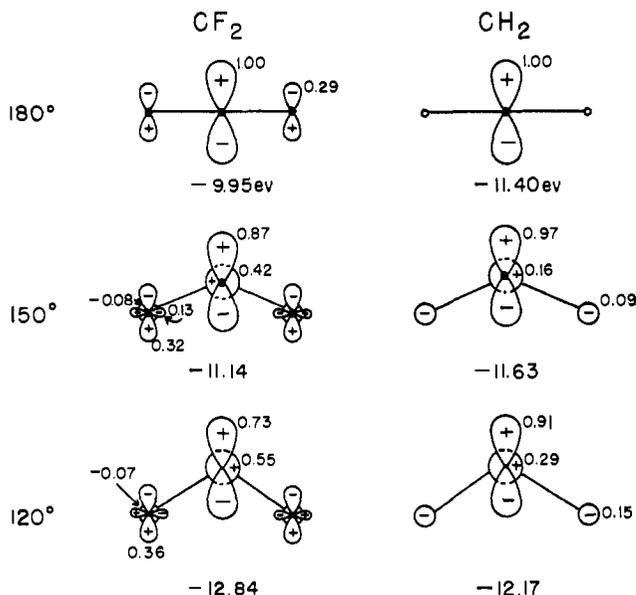


Figure 25. A comparison of the  $\text{CF}_2$  and  $\text{CH}_2$   $\sigma$  orbitals at three angles.

greatest part of the difference in the behavior of  $\text{CF}_2$  and  $\text{CH}_2$  lies in the  $\sigma$  level. For  $\text{CF}_2$  it is stabilized with bending at a much faster rate than in  $\text{CH}_2$ . Figure 25 shows the shapes and compositions of  $\text{CH}_2$  and  $\text{CF}_2$   $\sigma$  at 180, 150, and 120°. In a linear  $\text{CF}_2$  the degenerate pair of p orbitals is no longer pure p on the central carbon, as it is in  $\text{CH}_2$ , but instead is close to an antibonding allylic  $\pi$  orbital, with nodes between C and F. The destabilization is reflected in the high calculated energy of this orbital (-9.95 eV) compared to the energy of a free carbon 2p orbital (-11.40 eV). Thus one contribution to the great stabilization of  $\sigma$  on bending could be stated as follows: because the 180° orbital is destabilized, there is that much more to be gained by  $\text{CF}_2$  on bending. This however cannot be the whole story, for in fact in  $\text{CH}_2$  the electronic density in  $\sigma$  is less delocalized from the carbon atom than it is in  $\text{CF}_2$ , as bending proceeds. Thus in the linear form 1.83 out of 2.00 electrons in  $\text{CF}_2$  are on C (taking Mulliken gross atomic populations) and 2.00 out of 2.00 in  $\text{CH}_2$ . But at 120° bending  $\text{CF}_2$  has 1.55 on C while  $\text{CH}_2$  has 1.85.

### Fluoromethylmethylenes

We have also studied the conformations of trifluoromethylmethylene ( $\text{CF}_3\text{CH}$ ) and di(trifluoromethyl)methylene ( $\text{CF}_3\text{CCF}_3$ ) since the esr spectra of their triplet states have been detected in glasses. The results are presented in Figure 26. The positions of the  $\sigma^2$  minima are very close to those of the corresponding hydrocarbons  $\text{CH}_3\text{CH}$  and  $\text{CH}_3\text{CCH}_3$ . The  $\sigma^2$ - $\sigma p$  energy differences are smaller in the fluorocarbons, and this is to be contrasted with the opposite trend for fluorine substitution directly at the carbene site (see below). The  $\sigma p$  minima are very shallow and occur at  $\sim 155^\circ$  in  $\text{CF}_3\text{CH}$  and at  $165^\circ$  in  $\text{CF}_2\text{CCF}_3$ . The trend is precisely opposite to that inferred by a theoretical extrapolation of the observed zero-field splittings.<sup>20</sup>

(20) E. Wasserman, L. Barash, and W. A. Yager, *J. Amer. Chem. Soc.*, **87**, 4974 (1965).

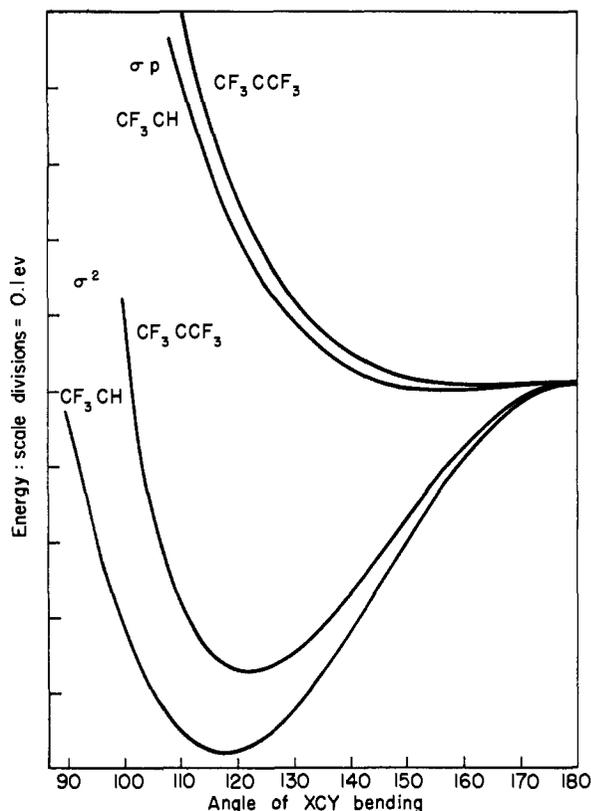
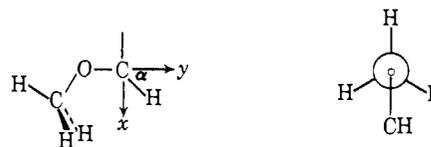


Figure 26. Configuration energies for  $\text{CF}_3\text{CH}$  and  $\text{CF}_3\text{CCF}_3$ .

### Methoxymethylene

The orientation of the molecule is shown below. The methyl group was maintained staggered with respect to the OCH bond. The parameters used were: distances



C-O 1.52, C-H 1.10 Å, COC angle tetrahedral. Figure 27 shows the energy curves for in-plane bending. Out-of-plane bending curves very nearly duplicate these curves, and are not shown. The  $\sigma^2$  configuration is bent, with minima at 105 and 257°. The two minima are of nearly identical energy and the potential surface connecting them has no unusual features. The  $\sigma p$  configuration also has two minima, at 115 and 242°.

It is interesting to note that in a number of ways methoxymethylene is intermediate between an alkylcarbene and a fluorocarbene. Thus both the  $\sigma^2$  and  $\sigma p$  minima are at smaller angles than in methylmethylene. The  $\sigma p$  minimum is quite deep and the  $\sigma^2$ - $\sigma p$  energy difference substantial. All of these phenomena are present in fluoromethylenes as well. The resemblance is not unexpected if electronegativity is a factor in the peculiarities of the fluoromethylene structure.

### General Observations

We have seen that given the relative position of  $p_0$  and  $p_1$  in a "linear" methylene it is possible to predict the general shape of the potential curve of the lowest singlet. The relative energy of  $p_0$  and  $p_1$  becomes then of prime interest. We have explored a number of ways

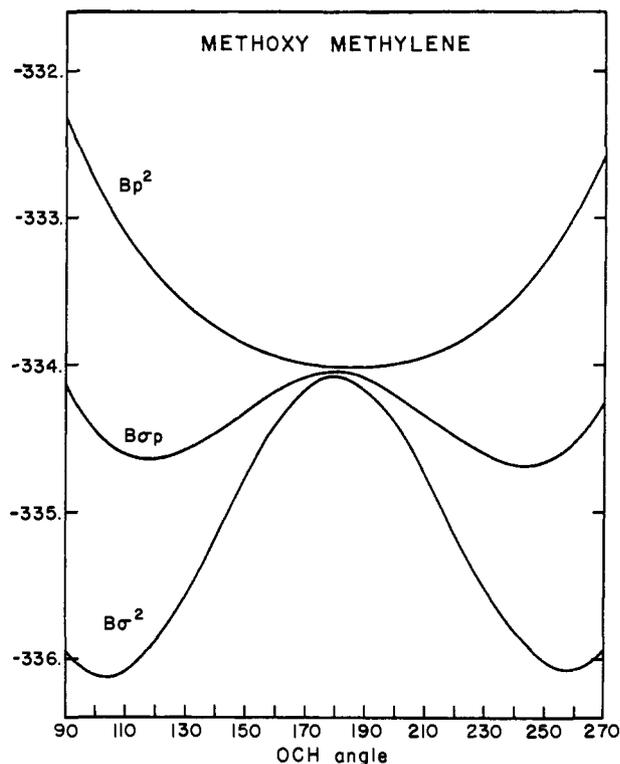


Figure 27. Configuration energies for in-plane bending of methoxy-methylene.

of stabilizing or destabilizing  $p_o$  with some success. Table V gives the location of  $p_o$  and  $p_i$  for some of the molecules we have considered.

Table V. The Energy of  $p_o$  and  $p_i$  Levels in "Linear" Conformations of Methylene<sup>a</sup>

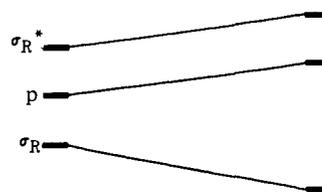
Molecule	$p_o$ , eV	$p_i$ , eV
HCH	-11.40	-11.40
HCCH <sub>3</sub>	-11.00	-11.00
CH <sub>3</sub> CCH <sub>3</sub>	-10.63	-10.63
HCOCH <sub>3</sub>	-10.92	-10.95
FCF	-9.95	-9.95
C <sub>6</sub> H <sub>5</sub> CH	-11.08	-10.90
CH <sub>2</sub> =CHCH	-11.16	-11.00
O=CHCH	-12.13	-11.21
NO <sub>2</sub> CH	-12.09	-11.16
HCCN	-11.73	-11.73
NCCCN	-11.93	-11.93
<i>c</i> -C <sub>6</sub> H <sub>5</sub> CH	-10.72	-11.01

<sup>a</sup> For conventions defining in plane and out of plane see text.

The following observations can be made. (1) The introduction of any substituent adjacent to the carbene tends to destabilize  $p_o$  and  $p_i$ . The exceptions result from additional interaction described in (3) below. (2) If the substituent carries a  $\pi$ -electron system it can discriminate in its interaction between  $p_o$  and  $p_i$ . (3)  $p_o$  is stabilized by a low-lying vacant level on the substituent, and destabilized by a high-lying occupied level.

The first point is apparent in the progression from methylene to methylmethylene and dimethylmethylene. It also shows up in methoxycarbene which appears to behave like the isoelectronic ethylmethylene. It even appears in phenyl- and vinylcarbene, but is reversed by an interaction of the third type in formylmethylene.

We think we can provide a quantum mechanical explanation of this. Consider the general molecule R-C-R and write down the energy levels before interaction: a p orbital on C and the  $\sigma$  and  $\sigma^*$  of R.



We now allow the orbitals to interact. The most general perturbation expression for the energy change in the  $i$ th level is

$$\Delta E_i = \sum_j \frac{H_{ij}^2}{E_i - E_j}$$

where  $H_{ij}$  is the matrix element of the perturbation and the coupling energy and the  $E_k$  are the noninteracted energy levels.  $H_{ij}$  is very roughly proportional to an overlap between orbitals  $i$  and  $j$ . From our experience with semiempirical molecular orbital calculations we have concluded that there are two factors which always push  $p$  to higher energy as a result of interaction with vicinal  $\sigma$  levels. (1) As a result of inclusion of overlap in the true wave functions  $\sigma^*$  is consistently more antibonding than  $\sigma$  is bonding. This is obvious in the hydrogen molecule and comes through to larger systems. Thus the denominator of the perturbation sum is smaller for the  $\sigma$  interaction than for the  $\sigma^*$ . (2) As a result of  $\sigma^*$  having more nodes than  $\sigma$ , the matrix element  $H_{p\sigma^*}$  is consistently smaller than  $H_{p\sigma}$ . Both factors operate to make the interaction with  $\sigma$  stronger than with  $\sigma^*$ , push  $p$  up in energy, and introduce a node between the  $p$  orbital and the adjacent atom orbitals. We clearly observe this node in all the cases mentioned above.

The second observation made above is fairly self-evident. There is no discrimination between  $p_o$  and  $p_i$  in "linear" methylene, ethylidene, cyanocarbene because the cylindrical symmetry does not allow it. The discrimination is clear when a  $\pi$ -electron system without cylindrical symmetry such as vinyl, formyl, nitro is attached. Two interesting cases are methoxy and cyclopropyl. In the former we hoped for a greater discrimination by the oxygen lone pair but found little. The latter presented us with more discrimination than vinyl and so was surprising.

The third observation follows from an understanding of the way in which the perturbation interaction operates. To depress a level a most efficient way is to introduce another level close by above it. To raise a level introduce another one available for mixing and located below it. It was this way of thinking which led us to try a formyl or nitro group to stabilize  $p_o$ , for a formyl group has a relatively low-lying  $\pi^*$  level<sup>21</sup> (the "center of gravity" of a C=O  $\pi$ -bond scheme lies below that of a C=C; our calculations applied to a CHO fragment give the C=O  $\pi$  level at -15.4 eV, the  $\pi^*$  at -9.9 eV). The resultant interaction with this higher level is strong enough so that no node, but a bonding in-

(21) A nitroso group is better still in this respect. The potential surface for nitrosomethylene is complicated and we plan to report on it in some detail later.

teraction, is found between the carbene  $p$  and adjacent orbitals. We find the lack of this node and clear stabilization for formyl-, nitro-, and cyanomethylenes. The cyanomethylenes are a case where as a result of required lack of discrimination between  $p_0$  and  $p_1$  both are stabilized. We think methoxycarbene is an example of a weak destabilization of  $p_0$  by interaction with a high-lying occupied orbital—the oxygen lone pair. Fluoro- and difluoromethylenes are more drastic examples of destabilization of  $p$  by occupied nonbonding orbitals.

The case of cyclopropyl is puzzling. This is the only clear-cut case (the other minor one is methoxymethylene) where  $p_0$  is destabilized more than  $p_1$ . A discriminating

interaction with the two levels is easy to accept if one is aware of the theoretical and experimental evidence for  $\pi$ -like orbitals in cyclopropane. But that these levels should destabilize  $p_0$  greatly implies that the interaction with the bonding Walsh level is considerably more efficient than with the antibonding. This is not apparent and we plan to investigate it further.

**Acknowledgment.** Our original interest in the electronic structure of methylenes was aroused by the exciting observations of E. Wasserman and coworkers. We are grateful for generous support of this work by the National Institutes of Health, the National Science Foundation, the Sloan Foundation, and the Chevron Research Company.

## Benzynes, Dehydroconjugated Molecules, and the Interaction of Orbitals Separated by a Number of Intervening $\sigma$ Bonds

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**Abstract:** From a variety of molecular orbital methods we have deduced significant and specific interactions among radical lobes in the same molecule separated by a number of intervening  $\sigma$  bonds. These are explored in detail for benzynes and didehydroconjugated molecules. The interaction (1) is shown to depend only on the orientation of the  $\sigma$  bonds between the radical lobes and the orientation of the lobes themselves, not on the specific molecule; (2) factors into direct (through-space) interactions proportional to the direct overlap and indirect (through-bond) coupling dependent on significant vicinal *cis* and, more important, *trans* overlaps; and (3) leads to the simpler splitting patterns as shown in the text by compounds 1–6 (Figure 3) where S and A beneath the geometrical outline indicate whether the symmetric (S,  $n_1 + n_2$ ) or the antisymmetric (A,  $n_1 - n_2$ ) combination of radical lobes is at lower energy. For a through-bond interaction over an odd number of  $\sigma$  bonds we give an argument for A falling naturally below S. The filling of A or S has a direct consequence on the stereochemistry of the reactions of the lowest singlet of these species.

Our calculations on benzynes and other dehydroconjugated molecules were stimulated by three experimental and one theoretical paper. In the first of these Berry and coworkers attempted to generate the *m*-benzyne and *p*-benzyne species.<sup>1</sup> At the same time we learned of some calculations on *o*-benzyne by Simmons.<sup>2</sup> The extended Hückel method makes it possible to do a calculation on any molecule desired, and the impedance to undertaking a series of calculations is not the ability to perform the computation but instead one's doubt as to the degree to which the calculation may be trusted.<sup>3</sup> To assuage this doubt it is useful to calibrate the reliability of the method for the series of molecules to be studied by examining how it performs for some known simpler member of the series. Unfortunately there was little that was exactly known about the geometry or electronic structure of even *o*-benzyne.<sup>4–6</sup>

(1) R. S. Berry, J. Clardy, and M. E. Schafer, *Tetrahedron Letters*, 1003, 1011 (1965).

(2) H. E. Simmons, to be published; also H. E. Simmons, *J. Amer. Chem. Soc.*, **83**, 1657 (1961).

(3) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); **40**, 2745, 2474, 2480 (1964); *Tetrahedron*, **22**, 521, 539 (1966).

(4) For recent reviews on the chemistry of benzynes, see R. Huisgen and J. Sauer, *Angew. Chem.*, **72**, 91 (1960); R. Huisgen in "Organometallic Chemistry," H. H. Zeiss, Ed., Reinhold Publishing Corp.,

Nevertheless some calculations were carried out on the three benzynes. The main point of interest in the results and the primary problem in the electronic structure of these species is the extent to which the two radical lobes, the two half-occupied lone pairs, interact or feel each other. As we will see below, such an interaction can be direct (through space) or through bond. The primary measure of interaction in quantum mechanics is the energy splitting between two levels which would be accidentally degenerate in the absence of any interaction. If one removes two hydrogens from a normal benzene molecule, there are left behind two  $\sigma$  orbitals, approximately nonbonding. Common preconception takes these as  $sp^2$  hybrids, but in fact their precise composition is (1) immaterial to the argument, and (2) in these calculations somewhat delocalized and quite different from  $sp^2$  locally. Let us simply call them  $n_1$  and  $n_2$

New York, N. Y., 1960, p 36; J. F. Bunnett, *J. Chem. Educ.*, **38**, 278 (1961).

(5) The intermediacy of benzyne was established by the work of J. D. Roberts, H. E. Simmons, L. A. Carlsmith, and C. W. Vaughan, *J. Amer. Chem. Soc.*, **75**, 3290 (1953), and R. Huisgen and H. Rist, *Naturwissenschaften*, **14**, 358 (1954).

(6) R. S. Berry, G. N. Spokes, and R. M. Stiles, *J. Amer. Chem. Soc.*, **82**, 5240 (1960); **84**, 3570 (1962), and references therein.