(18) Based on this idea, we may interpret the effect of λ_{irr} on $\phi_{C_2H_4}/\phi_{CP}$ (ϕ = quantum yield) presented in Table III of ref 8. The shorter λ_{irr} which is sufficient to raise CP up to the energy curve of its excited states initiates the photodissociation easily ($\phi_{C_2H_4}/\phi_{CP} \rightarrow$ large). On the other hand, the longer λ_{irr} gives the ground-state product of polymerization *plus* ethylene ($\phi_{C_2H_4}/\phi_{CP} \rightarrow$ small but nonzero). This nonzero $\phi_{C_2H_4}$ by the longer λ_{irr} may be explained as follows. The successive irradiation of the longer λ_{irr}, although not enough for the vertical excitation, would happen to make CP jump up from the electronically ground (but vibrationally excited) state to the $^1A_2$ curve resulting in the formation of the biradical intermediate.

On Geometry Predictions for Conjugated Free Radicals Containing Three π Electrons Using ab Initio MO Theory

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Abstract: Restricted Hartree–Fock STO-3G calculations were performed for the π state of the conjugated free radicals **1–8**. For **1–4**, geometry optimizations without configuration interaction included yielded structures with bond lengths appropriate to one single and one double bond, whereas a single potential minimum with near-equal distances is obtained when CI is included. Thus the "doublet instability" problem known previously for allyl **1** apparently is the rule rather than the exception. Calculations including CI for **5–8** indicated that the delocalization energy calculated by MO methods (ab initio or semiempirical) for a radical ZXY can be grossly in error unless the relative energies of the structures $Z{=}X{-}\dot{Y}$ and $\dot{Z}{-}X{=}Y$ are predicted accurately.

Semiquantitative results for the geometry and rotational barriers of most closed-shell organic molecules can be obtained from ab initio molecular orbital theory at its current "standard" level—i.e., by employing a single-determinant wave function and expanding each MO in terms of a minimal (or "double ζ") basis set.[1] In contrast, MO calculations for free radicals, such as allyl **1**, are fraught with difficulties due mainly to the "doublet instability" problem;[2] corresponding problems occur also for open-shell states of molecules containing an even number of electrons. The problem basically is that calculations using restricted Hartree–Fock (RHF) theory for three-center, three π electron systems usually overestimate the stability of structures containing one short and one long bond (e.g., **1a** and **1b**) relative to those with intermediate bond lengths (e.g., **1c**). The case of the allyl radical **1** has received detailed attention by Paldus and Veillard, who showed that the problem is one of correlation energy and not of basis set size.[2] Recent calculations for triplet states are those for HCCN by Harrison et al.[3] and for trimethylenemethane by Davidson and Borden.[4]

$H_2C{=}C(H){-}\dot{C}H_2$ **1a** $\quad H_2\dot{C}{-}C(H){=}CH_2$ **1b**

$\overline{H_2C{-}\dot{C}(H){-}CH_2}$ **1c**

In the present investigation, the predictions of ab initio RHF MO theory[5] both with and without configuration interaction for allyl **1**, for the free radicals **2–4**, **7**, and **8** isoelectronic with it, and for **5** and **6** are obtained to investigate further the doublet instability problem and to determine the delocalization energies of these systems. In the calculations, the minimal STO-3G basis set with standard molecular exponents[6] was used except where indicated. All results refer to the lowest π state only; the low-lying Σ states of **2–4**, **7**, and **8**, containing four π electrons with the unpaired electron in the σ framework, are discussed elsewhere.

For the radicals **1–4**, optimum heavy-atom bond lengths were determined separately in calculations without and with configuration interaction among all possible arrangements of the three electrons among three MOs (consistent with a net spin projection $M_S = +\frac{1}{2}$). We find that *two* potential minima with bonds of alternating length are predicted for **1**, **2**, and **3**, and that a single alternating-type minimum exists for **4**, in the single-determinant calculations (see Table I). In each case, however, such minima disappear and are replaced by a *single* structure of type **c**, with near-equal bond lengths between the conjugated atoms, when configuration interaction is included (see Table I). We conclude then that restricted open-shell MO theory will often predict (incorrectly) an "alternating" rather than a symmetrical structure for three π electrons, three π orbital networks and that CI among π-electron configurations is required to obtain meaningful results. Thus we suspect that the unsymmetrical structures predicted by single-determinant calculations for species such as NCO^+, NOC^+, NNC, CCN, and CCO (ref 7), for N_3 and N_3^+ (ref 8), and for HCC(H)O (ref 9) may be artifacts (but see the conclusions later regarding systems with different terminal groups).

$O{=}C(H){-}O\cdot$ **2a** $\quad \cdot O{-}C(H){=}O$ **2b** $\quad \overline{O{-}\dot{C}(H){-}O}$ **2c**

$HN{=}C(H){-}O\cdot$ **3a** $\quad H\dot{N}{-}C(H){=}O$ **3b** $\quad \overline{HN{-}\dot{C}(H){-}O}$ **3c**

$HN{=}N{-}O\cdot$ **4a** $\quad H\dot{N}{-}N{=}O$ **4b** $\quad \overline{HN{-}\dot{N}{-}O}$ **4c**

The role played by CI is illustrated best by the symmetrical-geometry allyl radical. Two-electron promotions allow for the correlation of the motion of the two electrons involved—for example, between the "spin-up" electron of the nonbonding MO and the "spin-down" electron of the bonding MO. Such correlation is important because these two electrons are predicted to be present simultaneously in the same p_π orbital (of a terminal atom) in 29% of the structures when the MOs are symmetric, if no CI is included. The participation by such unfavorable structures is reduced by about a factor of 2 by CI.

In RHF calculations *without* CI, the correlation between these two electrons can be achieved only if the molecule adopts "alternating" MOs, since this effectively localizes the non-

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Table I. Calculated Properties for π States of Conjugated Radicals XYZ[a]

method		$\overline{\mathrm{H_2C{-}\dot{C}(H){-}CH_2}}$[b]	$\overline{\mathrm{O{-}\dot{C}(H){-}O}}$[b,c]	$\overline{\mathrm{HN{-}\dot{C}(H){-}O}}$[d]		$\overline{\mathrm{HN{-}\dot{N}{-}O}}$[e]
RHF	R_{XY}	1.32	1.22	1.28	1.40	1.27
	R_{YZ}	1.47	1.42	1.41	1.22	1.44
	E(no CI)	−115.0196	−185.6041	−166.0707	−166.0623	−181.7889
	E(CI)	−115.0670	−185.6622	−166.1237	−166.1219	−181.8486
RHF +CI	R_{XY}	1.40	1.33	1.37		1.36
	R_{YZ}	1.40	1.33	1.35		1.38
	E(CI)	−115.0735	−185.6705	−166.1314		−181.8555

[a] All distances in Å, energies in au; all bond angles assumed 120° except as noted. All molecules assumed planar. [b] Another RHF minimum, with distances reversed, also exists. C-H distance in allyl assumed 1.080 Å. [c] Optimized ∠OCO = 121° (121°) at RHF (RHF + CI) level. Assumed C-H distance 1.100 Å. [d] RHF results from N. C. Baird and H. B. Kathpal, *J. Am. Chem. Soc.*, **98**, 7532 (1976). Optimized ∠NCO = 122°, ∠HNC = 105°, ∠HCN = 118° at RHF + CI. Assumed C-H, N-H distances of 1.105, 1.013 Å. [e] Optimized ∠NNO = 107° (107°); ∠HNN = 105° (103°). Assumed N-H distance 1.013 Å.

Table II. Structure and Energetics of $H_2\dot{C}XY$ and H_3CXY Systems by STO-3G + CI Calculations[a]

planar radical	$\overline{\mathrm{H_2C{-}\dot{C}H{-}CH_2}}$	$\overline{\mathrm{H_2C{-}\dot{C}{=}CH}}$	$\overline{\mathrm{H_2C{-}\dot{C}{=}N}}$	$\overline{\mathrm{H_2C{-}\dot{C}{-}O}}$	$\overline{\mathrm{H_2C{-}\dot{N}{-}CH_2}}$[b]
R_{C_1X}	1.40	1.43	1.44	1.40	1.38
R_{XY}	1.40	1.21	1.21	1.34	1.38
E(CI)	−115.0735	−113.8823	−129.7195	−150.3698	−130.8250
H_3CXY parent[c]					
R_{C_1X}	1.52	1.52	1.52	1.53	1.51
R_{XY}	(1.34)[d]	1.21	1.20	(1.26)[e]	1.32
E(CI)	−115.6950	−114.5128	−130.3513	−150.9880	−131.4456
ΔE (relative to propane, kcal mol^{-1})	17.3	11.7	10.9	19.3	17.9
rotation barrier,[c] kcal mol^{-1}	17.4			21.3 [18.8][f]	
C_1-H bond dissociation energy, kcal mol^{-1}	79.4	85.1	85.9	77.4	78.9

[a] All distances are in Å; all total energies are in au. The CXY framework of the parents, and all atoms of the radicals, is assumed planar. Bond angles assumed are 180° about dicoordinate carbon atoms, 120° about tricoordinate carbons, and 109.5° about tetracoordinate carbons. C-H bond lengths assumed are all 1.105 Å, except for the 1.080 Å used for allyl and for C_2-H and C_3-H in propene, 1.000 Å for C_3-H in $H_2\dot{C}C{\equiv}CH$ and $H_3CC{\equiv}CH$. [b] The CNC angle for the radical was optimized and found to be 115°; this same value was assumed in the parent CH_3NCH_2. [c] The CI for the parent systems and twisted radicals includes all configurations arising from the out-of-plane π electrons, and the in-plane π or lone-pair p electrons (if any), of X and Y. No CI is included in the calculations for propane or for the propyl radical. [d] The C=C distance is assumed to equal that calculated (with CI) for ethylene. [e] The C=O distance is assumed equal that calculated (with CI) for formaldehyde. [f] By 4-31G + CI calculations.

bonding electron of ψ_2 onto one of the terminal atoms, say C_1, and effectively restricts the two bonding electrons of ψ_1 to C_2 and C_3. Using our alternating, non-CI structure for allyl (see Table I), the two electrons discussed above are computed to appear simultaneously in the same atomic orbital in only 21% of the terms. Evidently the energy gain which the RHF calculations (incorrectly) associate with the net decrease in repulsion which occurs when the wave functions and bond lengths distort[10] is sufficient to overcome the simultaneous loss of bonding energy. However, when sufficient flexibility is introduced into the electronic wave function via CI and the motion of electrons thereby is properly correlated, the decrease in repulsion which accompanies alternation is insufficient to overcome the other factors, for average CC distances near the equilibrium value. (As pointed out by Paldus and Veillard,[2] though, an alternating structure is correctly predicted even by CI calculations when the average CC distance is large, so that the bonding energy goes to zero, since dissociation should occur to CH_2 + $HCCH_2$ rather than to the less stable "symmetrical" products H_2C + CH + CH_2.) We conclude then that structural studies for three electron, three orbital π networks should include CI among different π electron arrangements if spurious results are to be avoided.

To test the reliability of these methods in predicting stabilization energies for conjugated free radicals, calculations were performed for the π states of **5**–**8**; experimental energetics are available for these networks as well as for allyl. All the out-of-plane π or lone-pair p orbitals and electrons were included in the CI in geometry searches and in the final energy calculations for the radicals and for their parent closed-shell molecules which contain an additional hydrogen atom bonded to the terminal carbon C_1; the results are summarized in Table II.

$\dot{C}H_2{-}C{\equiv}CH$ $\dot{C}H_2{-}C{\equiv}N$

5a **6a**

$\dot{C}H_2{-}CH{=}O$ $\dot{C}H_2{-}N{=}CH_2$

7a **8a**

The stabilization energy ΔE in Table II for each $\dot{C}H_2X{=}Y$ free radical is defined as the difference between the C_1—H dissociation energies for propane, $CH_3{-}CH_2CH_3$, and for $CH_3{-}X{=}Y$. Experimentally the stabilization energy for allyl[11a] is ~11 kcal mol^{-1} compared to the value predicted here of 17. The calculated ΔE values for **5**, **6**, and **8** seem high by approximately the same amount, the experimental values being 8.6 ± 0.5, 6 ± 1, and ~14.5 kcal mol^{-1} compared to the predicted 12, 11, and 18, respectively.[11b-d] Since the calculated C_1-H bond energy of propane of 97 kcal mol^{-1} exceeds the experimental enthalpy of dissociation[12] by only 1 kcal mol^{-1}, the dissociation energies for the parents of **1**, **6**, and **8** are all too small by ~6 kcal mol^{-1}.

If the stabilization energy of the allyl radical is due entirely to conjugation, rotation by 90° about one carbon-carbon bond should require energy of about the same amount. Indeed the calculated rotation barrier[13] fortuitously agrees exactly with ΔE (see Table II. The agreement between the two quantities for **7** also is very good.) From rate constants, the free-energy barrier to rotation in the 1-methyl derivative of the allyl radical[14a] is ~21 kcal mol^{-1}. ESR measurements for allyl itself indicate that the rotational barrier is 17 kcal mol^{-1} at least.[14b] Thus our calculated barrier of 17 kcal mol^{-1} seems quite reasonable. However, the calculations provide no insight regarding the lack of agreement between the dissociation and rotation energy criteria of the stabilization energy.

The lesser stabilization energy of **6** compared to **1** and **8** is anticipated from both elementary MO and valence-bond theory since conjugation is most effective when the two extreme structures a and b are of equal energy, a circumstance which

$$\underset{a}{\dot{C}H_2{-}X{=}Y} \qquad \underset{b}{CH_2{=}X{-}\dot{Y}}$$

arises usually only if the terminal atoms are identical. On these grounds, the stabilization energy of radical **7** is expected to be small, since the combination of a carbon-oxygen double bond and a carbon-carbon single bond is known to be more stable than a carbon-oxygen single and a carbon-carbon double bond. In particular, the *experimental* enthalpy[14] for the reaction

$$H_2C{=}O + H_3C{-}\dot{C}H_2 \rightarrow H_3C{-}\dot{O} + H_2C{=}CH_2 \quad (1)$$

is +15.5 kcal mol^{-1}. It is surprising then to find that the structure for **7** has "intermediate" CC and CO lengths and that the calculated stabilization energy exceeds slightly that for allyl (see Table II). In contrast, the most recent experimental determination[15] of ΔE for **7** is 0–5 kcal mol^{-1}. (Even the largest value[15] previously proposed, 6 kcal, is less than that for allyl.) Apparently the difficulty here lies with the inability of minimal basis set calculations to predict properly the energetic superiority of C=O to C=C bonds. In particular, the energy predicted from STO-3G calculations *without* CI (but with all geometries optimized) for reaction 1 is *exothermic* by 14 kcal mol^{-1}, i.e., with C=C favored over C=O.[16] Recalculation of this difference with CI included (for the closed-shell molecules) reduces it to only 4 kcal mol^{-1}. Thus it is this incorrect prediction of near degeneracy for the a and b structures by STO-3G + CI calculations which is responsible for the incorrect prediction that conjugation is as important in **7** as in allyl. Improvement in the basis set to the extended "4-31G" level[17] should not solve the problem, as the energy difference predicted for reaction 1 using this basis set is −5 kcal without CI and −2 kcal with CI. Indeed recalculation of the barrier to rotation about the CC bond in **7** using the 4-31G basis (and the STO-3G + CI geometry) results in a decrease only from 21.3 to 18.8 kcal.[18]

For purposes of comparison, calculations for planar and twisted conformations of **1** and **7** were also performed by the semiempirical MINDO/3 method;[19] no CI was included, and open-shell MOs were determined using the "half-electron" procedure.[19] The stabilization energies so calculated for allyl and radical **7** are 6.1 and 2.2 kcal, respectively; the corresponding rotational barriers are 4.6 and −0.3 kcal. Thus MINDO/3 seems to *underestimate* slightly the energetic consequences of conjugation rather than to overestimate them as does the ab initio STO-3G + CI method. If the ab initio STO-3G RHF method is employed without CI, the ΔE and rotation barriers calculated for the (unsymmetrical) allyl radical are ~5 and ~6 kcal, respectively, i.e., quite similar to the semiempirical results. The MINDO/3 method, however, does successfully predict a symmetrical structure for allyl (CC bond lengths both 1.37 Å in the planar compared to 1.42 and 1.33 Å in the twisted) without the need for configuration interaction. For **7**, MINDO/3 predicts CC and CO bond lengths of 1.41 and 1.21 Å, respectively, i.e., very close to those expected for no conjugation. (The lengths in the twisted conformation are 1.43 and 1.20 Å, respectively.) This is consistent with the fact that MINDO/3 *overestimates* the stability of C=O + C—C relative to C—O + C=C (since the calculated energy difference for reaction 1 by this method is +34 kcal) and consequently underestimates the (small) amount of stabilization radical **7** possesses.

In conclusion, the analysis given above suggests that ab initio calculations for three-electron, three-orbital π radicals of the ZXY type (i.e., with different terminal atoms) should be viewed with great caution unless the theoretical method used has been shown to account properly for the energy difference between Z=X plus X—Y and Z—X plus X=Y bonds. In this connection, the reliability of the present calculations for **3**, **4**, and **6** as well as for **7** is open to question until the requisite thermochemical data for the bonds involved becomes available. For both YXY and ZXY radical types, the inclusion of some technique to account for the correlation between π electrons is required to obtain realistic geometries, although even then the stabilization due to conjugation can be overestimated significantly.

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References and Notes

(1) See, for example, the results in W. A. Lathan, L. A. Curtiss, W. J. Hehre, J. B. Lisle, and J. A. Pople, *Prog. Phys. Org. Chem.*, **11**, 175 (1974).

(2) See J. Paldus and A. Veillard, *Mol. Phys.*, **35**, 445 (1978), and references cited therein.

(3) J. F. Harrison, A. Dendramis, and G. E. Leroi, *J. Am. Chem. Soc.*, **100**, 4352 (1978).

(4) E. R. Davidson and W. T. Borden, *J. Am. Chem. Soc.*, **99**, 2053 (1977).

(5) C. C. J. Roothaan, *Rev. Mod. Phys.*, **32**, 179 (1960).

(6) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).

(7) A. A. Wu and Ch. Schlier, *Chem. Phys.*, **28**, 73 (1978).

(8) T. W. Archibald and J. R. Sabin, *J. Chem. Phys.*, **55**, 1821 (1971).

(9) N. C. Baird and K. F. Taylor, *J. Am. Chem. Soc.*, **100**, 1333 (1978).

(10) Distortion to an unsymmetrical geometry can occur even if little asymmetry is observed in the MOs at the symmetrical geometry, since electron localization may be feasible energetically only when the bonding energy of the alternating form is optimized.

(11) (a) The experimental stabilization energy quoted for allyl is the average of values for it and methylallyl as discussed in Z. B. Alfassi and D. M. Golden, *Int. J. Chem. Kinet.*, **5**, 295 (1973). The values quoted in Table II for all the other radicals except **5** refer to alkyl derivatives. (b) W. Tsang, *Int. J. Chem. Kinet.*, **10**, 687 (1978). (c) K. D. King and R. D. Goddard, *ibid.*, 7, 109 (1975). (d) A. T. Cocks and K. W. Eggar, *ibid.*, **4**, 169 (1972).

(12) Based upon data given by S. W. Benson, "Thermochemical Kinetics", Wiley, New York, 1975.

(13) The optimized C—C bond length for the twisted allyl radical is 1.50 Å, with R(C=C) assumed 1.34 Å; the CC and CO lengths for twisted **7** are 1.53 and 1.28 Å, respectively.

(14) (a) R. J. Crawford, J. Hamelin, and B. Strehlke, *J. Am. Chem. Soc.*, **93**, 3810 (1971); (b) P. J. Krusic, P. Meakin, and B. E. Smart, *ibid.*, **96**, 6211 (1974).

(15) F. Zabel, S. W. Benson, and D. M. Golden, *Int. J. Chem. Kinet.*, **10**, 275 (1978).

(16) Optimization of the geometry for **7** at the STO-3G level but *without* CI yields two minima, of which the $H_2C{=}CH{-}\dot{O}$ form is the more stable, as is anticipated from this analysis.

(17) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971).

(18) Unfortunately our present computational facilities and programs are not adequate to allow us to perform CI calculations for the parent system CH_3CHO (or for allyl itself) to determine the effect of basis set on dissociation energies.

(19) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1285 (1975), and papers following.