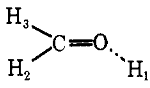
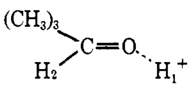
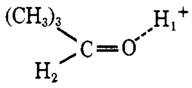
crease in oxygen atom repulsions was of major importance for the stability of the bent geometry relative to the linear structure. This result is independent of the form of the molecular orbitals, as the analysis was carried out on an atomic orbital basis set and thus is the same for both canonical and localized orbitals. A major disadvantage with the canonical orbitals is the difficulty in working with molecular orbitals which are so highly delocalized and the inconsistency of that description with the concept of an oxygen lone pair and OH bond in the adduct. With the localized molecular orbitals, however, such a description is possible on the molecular level. In the earlier analysis, it was found that the electron–electron repulsions due to electron density in oxygen atomic orbitals decreased by 291 kcal/mol on passing from the linear to the bent structure. (The *total* one-center energy change for oxygen was computed to be -16 kcal/mol by the CNDO/2 method used earlier; for the INDO method used here to generate the localized orbitals, the oxygen one-center energy change is computed to be -17 kcal/mol.) Using the (four) localized *molecular* orbitals originating at the oxygen atom, the decrease in repulsion energy which can be attributed to those electrons on passing from linear to bent geometry is 50 kcal/mol. The change in total electron repulsions for the molecule turns out to be only -17 kcal/mol, and the difference in total energy is only 11 kcal/mol, so the decrease in repulsions about the oxygen is seen to be a major factor in the stability of the bent geometry.

Nmr Coupling Constants. In the previous report[1] on formaldehyde and acetaldehyde adducts with the proton, it was concluded on the basis of the CNDO/2 total molecular energies that the acetaldehyde adduct structure with the CH and OH^+ bonds cis to each other was the more stable. This was supported by the agreement of J_{cis}/J_{trans} from experimental results and those ratios computed from CNDO/2 bond indices. The agreement held for the cis–trans coupling in H_2COH^+ and both the allylic and ethylenic couplings in both isomers of CH_3CHOH^+. To further confirm these results, the Fermi contact coupling constants were computed by the method for molecular orbitals as developed by Pople.[17] The INDO method was used with the results, shown in Table VIII, confirming the assignment of the *cis*-acetaldehyde adduct structure as the more stable conformer.

Table VIII. $J_{H,H}$ for H_2COH^+ and CH_3CHOH^+ [a]

		
$J_{12} = 9\ (9)$ $J_{13} = 29\ (21)$ $J_{23} = 19\ (22)$	$J_{12} = 14\ (9)$ $J_{13} = -1\ (\sim 0)$	$J_{12} = 30\ (20)$ $J_{13} = 1\ (1)$

[a] Units are hertz. Experimental values in parentheses.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We wish to thank Dr. K. G. Kay for valuable discussions.

(17) J. A. Pople and D. P. Santry, *Mol. Phys.*, 8, 1 (1964); A. H. Cowley and W. D. White, *J. Amer. Chem. Soc.*, 91, 1917 (1969).

Ground States of σ-Bonded Molecules. XV.[1] Barriers to Rotation about Carbon–Carbon Bonds[2]

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Abstract: Barriers to rotation about C—C and C=C bonds in a number of compounds have been calculated by the MINDO/2 method.

Previous papers of this series[1,3] have shown that the MINDO/2 method[3a,b] can give good estimates of the ground-state properties of molecules and for the potential surfaces for chemical reactions. One of the problems studied[3a] was the barrier to rotation about a C—C or C=C bond; estimates of the barrier heights for ethane, ethylene, and the cumulenes were in reasonable agreement with experiment.

Since this is a problem of current interest, and since the original calculations were carried out using a set of parameters that have been superceded,[3b] we have repeated them and extended them to a wide variety of additional molecules. Since the results are in reasonable agreement with the scanty evidence available and also lead to interesting predictions, we are reporting them in the hope of stimulating appropriate experimental studies.

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(1) Part XIV: M. J. S. Dewar and D. H. Lo, *J. Amer. Chem. Soc.*, **93**, 7201 (1971).

(2) This work was supported by the Air Force Office of Scientific Research through Contract No. F44620-70-C-0121 and by the Robert A. Welch Foundation.

(3) (a) M. J. S. Dewar and E. Haselbach, *J. Amer. Chem. Soc.*, **92**, 590 (1970); (b) N. Bodor, M. J. S. Dewar, A. Harget, and E. Haselbach, *ibid.*, **92**, 3854 (1970); (c) M. J. S. Dewar, E. Haselbach, and M. Shanshal, *ibid.*, **92**, 3505 (1970); (d) M. J. S. Dewar and J. S. Wasson, *ibid.*, **92**, 3506 (1970); (e) N. Bodor and M. J. S. Dewar, *ibid.*, **92**, 4270 (1970); (f) A. Brown, M. J. S. Dewar, and W. W. Schoeller, *ibid.*, **92**, 5516 (1970); (g) M. J. S. Dewar and J. S. Wasson, *ibid.*, **93**, 3081 (1971).

Table I. Heats of Formation at 25° (ΔH_f) and Geometries of Ethane and Propene Conformers

Molecule	ΔH_f, kcal/mol, calcd (obsd)[a]	Bond lengths, Å, calcd (obsd)[b]
Ethane (staggered)[c]	−24.70 (−20.24)	C—C, 1.487 (1.534); C—H, 1.107 (1.093)
Ethane (eclipsed)[c]	−22.81 (−17.3)	C—C, 1.494; C—H, 1.111
Propene (eclipsed)	0.91 (4.88)	C=C, 1.315 (1.353);[d] C—C, 1.463 (1.488);[d] C—C—C, 129 (124.3)[d]
Propene (staggered)	2.25 (6.9)	C=C, 1.327; C—C, 1.466

[a] F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun, and G. C. Pimentel, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953. [b] L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, No. **11** (1958); No. **18** (1965). [c] Unpublished work by Dr. R. Bingham. [d] Angle, degrees: D. R. Lide, Jr., and D. Christensen, *J. Chem. Phys.*, **35**, 1374 (1971).

Table II. Heats of Formation (ΔH_f), Rotational Barriers and Frequencies, and Geometries of Cumulenes

Molecule	ΔH_f, kcal/mol at 25°, calcd (obsd)[a]	Rotational barrier, kcal/mol, calcd (obsd)[b]	Rotational frequency, cm^{-1}, calcd (obsd)[b]	Bond lengths, Å calcd (obsd)[c]
Ethylene	13.43 (12.50)	53.46 (65.0)	801 (1027)	C=C, 1.310 (1.338); C—H, 1.096 (1.083)
Allene	41.57 (45.92)	36.73	681 (865)	C=C, 1.291 (1.3-1.34); C—H, 1.091 (1.07-1.08); H—C—H, 113.8° (111-117)°
Butatriene	73.34	31.60 (30.0)	611 (736)	C(1)=C(2), 1.293 (1.318[b]); C(2)=C(3), 1.274 (1.283[b]); C—H, 1.091; H—C—H, 113.4°
Pentatetraene	103.02	24.84	543	C(1)=C(2), 1.292; C(2)=C(3), 1.272; C—H, 1.091; H—C—H, 114.2°
Hexapentaene	134.01	22.05 (20.0)	516	C(1)=C(2), 1.286; C(2)=C(3), 1.276; C(3)=C(4), 1.282; C—H, 1.091; H—C—H, 110.0°

[a] See Table I, footnote *a*. [b] For references, see M. J. S. Dewar and E. Haselbach, *J. Amer. Chem. Soc.*, **92**, 590 (1970). [c] See Table I, footnote *b*. Bond angles in degrees.

The calculations were carried out by the standard MINDO/2 method, using the parameters of part X.[3b] The energy was calculated for various values of the angle of twist (θ), ranging from 0 to 90° for symmetrical ethylene derivatives and 0 to 180° for unsymmetrical ones. In the case of ethane and propene, calculations were carried out for the eclipsed and staggered forms. In each case the energy was minimized with respect to all the other coordinates, using a program written by Dr. A. Brown and based on the Simplex method.[4] The MINDO/2 method gives heats of atomization; for convenience, these were converted[3] to heats of formation at 25°, using experimental values for the heats of formation of atoms.

Results and Discussion

While our main concern was with barriers to rotation about C=C bonds, we also carried out calculations for ethane and propene in the conformations known to correspond to the ground state and transition state for rotation; the results are shown in Table I.

The barrier to rotation in ethane has been estimated calorimetrically (2.875 kcal/mol[5]) and from infrared spectroscopy (3.030,[6a] 2.928[6b] kcal/mol). Our results correctly predict the ground state to be staggered; while the calculated barrier height is too low (1.89 kcal/mol), it is higher than the earlier MINDO/2 value (1.4 kcal/mol[3b]), this being based on an assumed tetrahedral geometry.

In propene we correctly predict the stable conformation to be C=C eclipsed; the calculated barrier height (1.34 kcal/mol) is again somewhat less than experiment (1.950–2.039 kcal/mol[7]).

The MINDO/2 values for barrier heights are clearly inferior to those given by the STO-3G SCF method (3.33 and 1.55 kcal/mol, respectively[8]). Barriers to rotation about single bonds present an exceptionally favorable case for *ab initio* SCF methods, since the bonding does not change significantly during rotation; one might therefore expect the correlation energy to be essentially constant.[9]

Table II lists calculated heats of formation, geometries, barriers to rotation, and torsional vibration frequencies for ethylene and the lower cumulenes. The heats of formation, geometries, potential curves, and barriers to rotation are very similar to those given by the earlier treatment and are likewise in good agreement with experiment (Table II). The torsional vibration frequencies are, however, less than those calculated previously and experiment. We suspect that an error was made in part IX[3a] in the calculation of torsional vibration frequencies from the potential curves.

(4) J. A. Nelder and R. Mead, *Comput. J.*, 7, 308 (1964).

(5) K. S. Pitzer, *Discuss. Faraday Soc.*, No. **10**, 66 (1951).

(6) (a) D. R. Lide, Jr., *J. Chem. Phys.*, **29**, 1426 (1958); (b) S. Weiss and G. E. Leroi, *ibid.*, **48**, 962 (1968).

(7) W. G. Fately and F. A. Miller, *Spectrochim. Acta*, **19**, 611 (1963); D. R. Lide, Jr., and K. S. Pitzer, *J. Res. Nat. Bur. Stand.*, **37**, 163 (1946); D. R. Lide, Jr., and D. E. Mann, *J. Chem. Phys.*, **27**, 868 (1957); E. Hirota, *ibid.*, **45**, 1984 (1966); K. D. Möller, A. R. DeMeo, D. R. Smith, and L. H. London, *ibid.*, **47**, 2609 (1967).

(8) L. Radom and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 4786 (1970), and references cited therein.

(9) See L. Radom, W. J. Hehre, and J. A. Pople, *ibid.*, **93**, 289 (1971).

While *ab initio* SCF calculations lead to good estimates of barriers to rotation about single bonds, those for double bonds are much too large.[8] It is of course well known that bond dissociation processes cannot be described in terms of an orbital approximation using single Slater determinants. It is essential to include at least the first doubly excited configuration in order that dissociation may lead to a pair of radicals rather than to a hybrid of radicals and ions. Since the transition state for rotation in ethylene or a cumulene can be represented as a biradical, it seems reasonable to suppose that the failure of *ab initio* methods may be due to neglect of essential configuration interaction, and it has been suggested that the use of MINDO/2 in this connection is theoretically unsound for the same reason. Since this is an important point and one that has arisen in other connections, a detailed discussion seems called for.

The philosophy underlying the semiempirical SCF–MO approach is to take electron correlation into account by suitable choice of parameters rather than by configuration interaction (CI). As a general rule, inclusion of CI in MINDO/2 would be a gross error, since one would then be allowing for electron correlation twice over. Similar problems arose in attempts[10] to treat radicals by an open-shell SCF treatment, using parameters appropriate to closed-shell systems; we were forced to develop[10] a closed-shell treatment of radicals to avoid this complication. The success of MINDO/2 shows that this approach to electron correlation is in fact feasible, all the ground-state properties of molecules being reproduced with surprising accuracy using a single set of parameters. The method does fail in extreme situations where the balance between ionic and covalent structures is very greatly disturbed; this is the case for pairs of isolated radicals ($R\cdot \ \cdot R$) where the contribution of the corresponding ionic structures (R^+R^-) is negligible. Here one must include the first doubly excited configuration in order to cancel the contribution of such ionic structures; we have found that with this single modification, MINDO/2 can account well for bond dissociation processes.

Similar problems arise in the case of biradicals with widely separated radical centers (*e.g.*, $\cdot CH_2CH_2CH_2CH_2\cdot$), where there are effectively two unpaired electrons centered on different atoms. The heats of formation given by MINDO/2 in such cases are much too high (*cf.* ref 3a) but can again be brought into agreement with experiment by inclusion of the first doubly excited configuration.

The situation is different in the case of the transition state for rotation about the CC bonds in a cumulene because the two electrons in question now occupy MO's covering the same set of carbon atoms. Here the specific correlation effects characteristic of biradicals should be absent and it is therefore not surprising that MINDO/2 gives good estimates of the barriers to rotation. As a check, we have tried including CI in the case of ethylene, including the lowest doubly excited configuration; the effect on the rotational barrier was small, in contrast to the large effect of CI on the calculated heats of formation of genuine biradicals. This suggests that the correlation effects in the transition states for rotation are not appreciably different from those in normal molecules and are consequently well taken care of by our parametric approach.

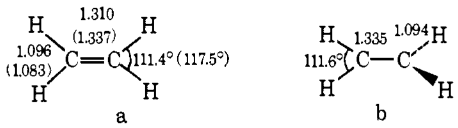

Figure 1. Calculated (observed) bond lengths (Å) and bond angles for ethylene (a) in its ground state and (b) with the methylene groups twisted through 89°.

It should be noted that this is not the case for *ab initio* SCF methods where correlation effects are entirely neglected. Thus inclusion of the first doubly excited configuration lowers the calculated barrier to rotation in ethylene from 138 to 83 kcal/mol.[11] The total neglect of CI in single-configuration *ab initio* SCF treatments can clearly lead to chemically unacceptable errors.

These arguments are further supported by the magnitude of the barrier to rotation in ethylene. If the transition state were a biradical, $\cdot CH_2CH_2\cdot$, the barrier should be equal to the difference between the bond energies for C=C and C—C bonds. In fact, the barrier (65 kcal/mol) is much greater than this difference (35.0 kcal/mol[12]). The discrepancy is indeed even greater than this because the biradical must be stabilized by hyperconjugation.[13] Clearly, the transition state for rotation about the C=C bond in ethylene cannot properly be described, or treated, as a simple biradical.

Figure 1 shows the calculated geometries for ethylene in its ground state and with the methylene groups twisted through 89°. The latter structure should be essentially identical with the transition state for rotation; owing to orbital degeneracy, problems arose in carrying out calculations for the exactly perpendicular configuration.

Note that the CC bond length is little greater in the transition state than in the ground state; the CC π-bond order in the former is correspondingly large (0.677, compared with 1.062 in the ground state), confirming the suggestion[13] that there should be very strong hyperconjugation between the carbon 2p AO's and the adjacent methylene groups in the transition state.

Table III shows calculated heats of formation and rotational barriers for a number of ethylene derivatives (**1–10**). The heats of formation agree quite well with the limited experimental data available, as do the rotational barriers for *trans*-2-butene (**1**) (62.8 kcal/mol[14]) and *trans*-1,3,5-hexatriene (**2**) (43.3 kcal/mol[15]). Note that in the case of **2** our calculated value is too high, whereas in ethylene and **1** our values are too low; the transition state for rotation in **2** should approximate to the resonance-stabilized biradical **3**, in which two unpaired electrons occupy MO's that do not overlap effectively; correlation effects should be correspondingly more important than in ethylene or **1** and our estimate of the barrier correspondingly too large.

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(10) M. J. S. Dewar, J. A. Hashmall, and C. G. Venier, *J. Amer. Chem. Soc.*, 1953 (1968).

(11) (a) U. Kaldor and I. Shavitt, *J. Chem. Phys.*, 48, 191 (1968); (b) R. J. Buenker, *ibid.*, 48, 1368 (1968).

(12) M. J. S. Dewar and C. de Llano, *J. Amer. Chem.Soc.*, 91, 789 (1969).

(13) R. S. Mulliken and C. C. J. Roothaan, *Chem. Rev.*, 41, 219 (1947).

(14) B. S. Ravinovitch and K. W. Michel, *J. Amer. Chem. Soc.*, 81, 5065 (1959).

(15) W. von E. Doering, personal communication.

Table III. Calculated (Observed) Heats of Formation (ΔH_f) Bond Lengths, and Barrier Heights to Rotation about C=C Bonds in Ethylene Derivatives

Compound	ΔH_f, kcal/mol at 25°	Rotational barrier, kcal/mol	Bond lengths, Å, calcd (obsd)[b]
Propene	0.91 (4.88[a])	53.5	C=C, 1.315 (1.353); C—C, 1.463 (1.488)
cis-2-Butene	−10.03 (−1.67[a])	50.1	C=C, 1.335 (1.38); C—C, 1.462 (1.54); C(1)—H, 1.120 (in plane), 1.107 (out of plane); C(2)—H, 1.106; C—H (obsd), 1.06; C—C—C, 126.7°
1	−12.45 (−2.67[a])	52.5 (62.8[c])	C—C, 1.334 (1.339); C—C, 1.473 (1.52), C(1)—H, 1.107 (in plane), 1.104 (out of plane) (1.06); C—C—C, 127° (123°)
Isobutylene	−7.38 (−4.04[a])	51.2	C=C, 1.329 (1.34); C—C, 1.481 (1.54), C(1)—H, 1.097 (1.09); C(3)—H, 1.113 (in plane) 1.109 (out of plane) (1.09); C(3)-C(2)—C(4), 117.4° (111.5°)
trans-**2**	41.13 (49)[d]	47.5 (43.3)[e]	C(1)=C(2), 1.319; C(3)=C(4), 1.325; C(2)—C(3), 1.444; C—H, 1.103; C(1)—C(2)—C(3), 125.6°; C(2)—C(3)—C(4), 126.0°
cis-**2**	42.54	46.1	C(1)=C(2), 1.318; C(3)—3(4), 1.333; C(2)—C(3), 1.449; C—H, 1.104; C(1)—C(2)—C(3), 126.1°; C(2)—C(3)—C(4), 125.8°
4	67.33 (69[d])	51.1	C=C, 1.323 (1.34); C≡C, 1.191 (1.20); C—C, 1.404 (1.448); C(1)—H, 1.067 (1.06); C(3)—H, 1.106 (1.07); C(4)—H, 1.091 (1.07); C(2)—C(3)—C(4), 123.8° (123.0°)
5	14.94	48.1	C(1)—C(2), 1.461; C(2)—C(3), 1.481; C(1)=C(4), 1.306; C(4)—H, 1.097; C(2)—H, 1.105
6	16.16	43.4	C(1)-C(2), 1.453; C(2)—C(3), 1.494; C(1)=C(1′), 1.304; C—H, 1.102
7	62.02	30.6	Figure 2
8	118.57	35.4	Figure 2
9	43.52 (47.5[f])	45.6	Figure 3
10	88.23	26.8	Figure 3

[a] See footnote *a*, Table I. [b] See footnote *b*, Table I. Bond angles, degrees. [c] Reference 14. [d] J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxel, and F. H. Field, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Ions," NSRDS-NBS 26, National Bureau of Standards, Washington, D. C., 1969. [e] W. von E. Doering, personal communication. [f] N. C. Baird, *Mol. Phys.*, **18**, 39 (1970).

Table IV. Changes in π-Bond Order and Bond Length on Rotation about CC Bonds

Compound	Total π-bond order: Ground state	Transition state	Difference	Bond length, Å: Ground state	Transition state	Difference
$CH_2{=}CH_2$	1.062	0.677	0.385	1.310	1.335	0.025
5	1.082	0.755	0.327	1.306	1.326	0.020
6	1.184	0.961	0.223	1.304	1.322	0.018


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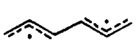
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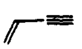
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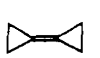
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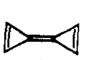
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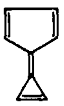
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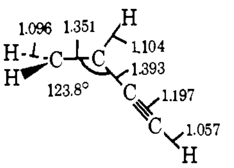

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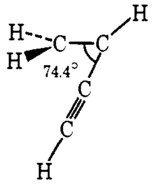


12

Our conclusions for vinylacetylene (**4**) differ somewhat from those reached by Radom and Pople[8] from their STO-3G calculations. We predict the barrier to rotation about the C=C bond to be significantly less than in ethylene, whereas their values were almost identical (138 kcal/mol). Also, we predict the transition state to have a normal geometry **11**, whereas Radom and Pople predict it to have a folded π-complex structure **12**. Since MINDO/2 in general overestimates the stability of small rings, and since it gives absolute values of barriers that are in much better agreement with experiment than those of *ab initio* SCF methods, we suspect that our conclusions may be more reliable.

The calculated barrier heights for methylenecyclopropane (**5**) and cyclopropylidenecyclopropane (**6**) indicate a progressive stabilization of the transition state by *ca.* 5 kcal/mol per cyclopropane ring. This is not surprising in view of the strong hyperconjugative interactions in the case of the transition state for ethylene, because introduction of a cyclopropane ring should enhance such interactions. This is indicated by Table IV, which shows the total π-bond orders and calculated CC bond lengths for various ethylene derivatives and the corresponding transition states for rotation about the C=C bonds. The changes in CC bond order and bond length, on passing to the transition state, decrease in the series ethylene > **5** > **6**, while the total CC π-bond orders increase.

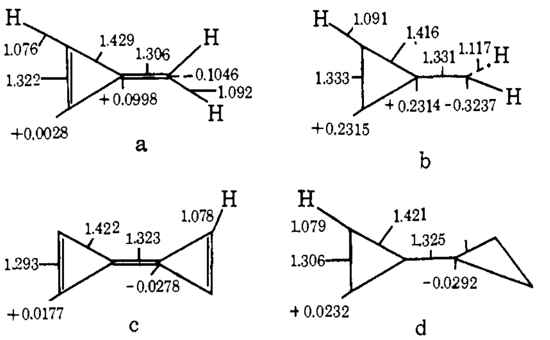


Figure 2. Formal charges on carbon, and calculated carbon–carbon bond length: (a) in **7**, (b) in the transition state for rotation about the exocyclic bond in **7**, (c) in **8**, (d) in the transition state for rotation about the interannular bond in **8**.

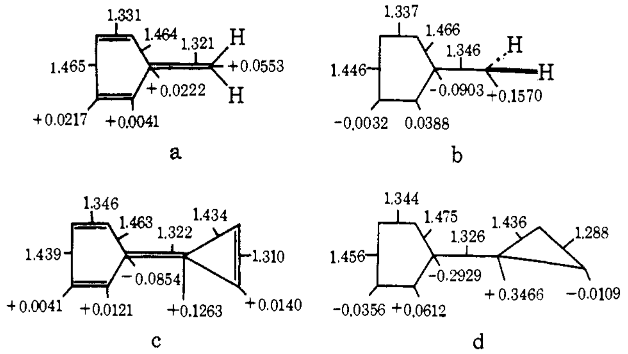
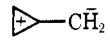


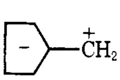
Figure 3. Formal charges and calculated bond lengths in (a, b) fulvene (**9**) and the transition state for rotation about the exocyclic bond; (c, d) calicene (**10**) and the transition state for rotation about the interannular bond.

Introduction of a cyclopropene ring into ethylene produces a dramatic decrease (23 kcal/mol) in the calculated barrier height; here, however, introduction of second cyclopropene ring leads to a small *increase* (5 kcal/mol) rather than a further decrease. The reason for this can be seen from the calculated formal charges (Figure 2a,b). The transition state is highly polar in the sense indicated by the zwitterionic structure



In confirmation, only one of the π MO's of the cyclopropenium moiety is occupied. The transition state is therefore stabilized by the effective presence of an aromatic cyclopropenium ion. In the case of **8**, there would be no advantage in this, since the second ring would have to adopt a structure corresponding to the antiaromatic cyclopropyl anion; the calculated formal charges (Figure 2c,d) indicate that the transition state is effectively nonpolar, corresponding formally to a pair of nonaromatic[16] cyclopropenyl radicals.

The formal charges in the transition state for rotation about the exocyclic bond in fulvene **9** (Figure 3b) indicate that it does not have a zwitterionic structure. This is not surprising, since aromatic stabilization decreases with increasing ring size and is less for anions than for cations; in the case of **9**, the difference in resonance energy between the C_5 anion and radical is apparently insufficient to overcome the effect of charge separation in the zwitterionic structure



This conclusion is supported by the orbital occupancy in the transition state and by the fact that the barrier for **9** differs from that for ethylene by about half the corresponding difference for **6**.

As one might expect on this basis, the calculated barrier height for calicene (**10**) is very low indeed (26.8 kcal/mol), and the calculated formal charges and bond lengths (Figure 3d) correspond to a zwitterionic structure for the transition state. This is confirmed by a study of the corresponding eigenvectors; three π MO's of the C_5 moiety are occupied, but only one of the cyclopropenium unit.

No barrier heights have as yet been reported for **7**–**10**. In the case of 6-dimethylaminofulvene, solvent and substituent effects indicate the transition state to be zwitterionic;[17] here, of course, the −E dimethylamino group would be expected to stabilize the zwitterionic structure and the observed barrier is correspondingly low (27 kcal/mol[17]).

If the transition state for calicene is zwitterionic, the barrier should be lowered by electron-releasing substituents in the three-membered ring and electron-withdrawing substituents in the five-membered one. The barrier to rotation in 1-formyl-5,6-di-*n*-propylcalicene (18–19.4 kcal/mol[18]) is, as expected on this basis, less than our calculated value for calicene itself.

Calculations have also been carried out for some other systems, in particular the allyl cation and amides.

The calculated heat of formation of allyl cation (225.9 kcal/mol) is in reasonable agreement with experiment (216 kcal/mol[19]), and the calculated CC bond length (1.364 Å) seems reasonable. Difficulties arose, however, in attempts to calculate the transition state for rotation owing to a known failing of MINDO/2, *i.e.*, the tendency of hydrogen atoms in potentially nonclassical cations to move into bridging positions. Fixing the bond angles at 120° gave a barrier height of 13.0 kcal/mol, somewhat less than the values reported[20] for *cis,cis-* (17.5 kcal/mol) and *cis,trans-* (24.0 kcal/mol) 1,3-dimethylallyl cations ion solution. The agreement is probably acceptable in view of the uncertainty of the (undoubtedly large) effects of solvation and the methyl substituents.

In the case of amides, however, there is a clear and serious discrepancy between the calculated (*ca.* 5 kcal/mol) and observed (*ca.* 20 kcal/mol) barriers. We suspect that this is due to an inherent failing[3b] of the INDO approximation, *i.e.*, its inability to account for the dipole fields of lone pairs of electrons in second-row atoms. This difficulty could be overcome only by explicitly including one-center overlap, *i.e.*, by using

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(16) See M. J. S. Dewar, *Tetrahedron, Suppl.*, No. 8, 75 (1966); "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969, p 225.

(17) A. P. Downing, W. D. Ollis, and I. O. Sutherland, *J. Chem. Soc. B*, 111 (1969).

(18) A. S. Kende, P. T. Izzo, and W. Fulmor, *Tetrahedron Lett.*, 3697 (1966).

(19) F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun, and G. C. Pimentel, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbon and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953.

(20) P. von R. Schleyer, T. M. Su, M. Saunders, and J. C. Rosenfeld, *J. Amer. Chem. Soc.*, **91**, 5174 (1969).

the NDDO approximation instead of INDO. While we are studying the parametrization of NDDO, the results are not yet sufficient to show whether the advantages gained compensate for the additional computation time (greater by a factor of 2–3 over MINDO/2).

Ground States of σ-Bonded Molecules. XVI.[1] The Rearrangement of Methyl Isocyanide to Acetonitrile[2]

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Abstract: The MINDO/2 method has been used to calculate the reaction path for the conversion of methyl isocyanide into acetonitrile. The calculated heat of reaction and activation energy are in reasonable agreement with experiment as also are the geometries and heats of formation of reactant and product. The reaction is predicted to involve a stable triangular intermediate with the properties expected of a π complex rather than an ion pair.

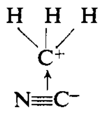
Some time ago one of us interpreted[3] the thermal conversion of methyl isocyanide (**1**) to acetonitrile (**2**) as an intramolecular rearrangement involving an intermediate π complex (**3**), *i.e.*, a species in which methyl is linked to the CN moiety by a three-center covalent bond. According to the π-complex theory[3,4] the bond in **3** should, so far as the methyl group is concerned, be no different in kind from the normal two-center bond CX in a methyl derivative H_3CX; the migrating methyl group should therefore on this basis retain its stereochemistry during the reaction and the intermediate phases should not differ much in polarity from the starting material and reactant.

$H_3C{-}{}^{+}N{\equiv}\bar{C}$

1

$N{\equiv}C{-}CH_3$

2



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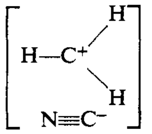


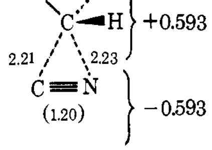
4

The rearrangement of **1** to **2** has been studied in detail by Schneider and Rabinovitch;[5] the reaction takes place homogeneously in the gas phase, following kinetics characteristic of a unimolecular process. Rabinovitch, *et al.*, concluded that the migration of methyl must be intramolecular, the transition state having a triangular geometry (*cf.* **3**).

This conclusion was supported by Casanova, *et al.*,[6] who showed that optically active derivatives of **1** rearrange with complete retention of configuration of the migrating group. Further light was shed on the nature of the transition state by a study of alkyl derivatives of **1**, the relative rates of rearrangement of methyl, ethyl, isopropyl, and *tert*-butyl isocyanides being 5.6:7.8:2.6:1.0; the lack of any consistent trend along the series suggests that the transition states must differ little in polarity from the reactants and also that the migrating carbon retains its tetrahedral geometry.

These results clearly provide strong support for the π-complex mechanism.

Recently Van Dine and Hoffmann[7] have studied the rearrangement of **1** to **2** by the "extended Hückel" method, assuming a fixed CN bond length (1.20 Å) and fixed geometries for the methyl group. When the latter was assumed to remain pyramidal throughout, the transition state was predicted to have the geometry indicated below (CN and CC distances (Å), and formal charges on methyl and CN, calculated by Van Dine and Hoffmann[7] for the rearrangement **1** → **2**), the methyl–carbon and methyl–nitrogen distances being similar and very long, with large formal charges on the methyl and CN groups.



Since this result seemed to suggest that the reaction was tending to pass through an intermediate ion pair **4**, they recalculated the energy of the symmetrical intermediate, assuming the methyl group to be planar, for various methyl–CN distances. Then equilibrium methyl–CN distance increased from *ca.* 2.1 Å to *ca.* 2.5 Å and the energy at the minimum decreased by *ca.* 0.4 eV. While they do not quote charges for this structure, it seems reasonable to assume that it must have corresponded closely to **4**.

The procedure used by Van Dine and Hoffmann is admittedly far from reliable, leading to predicted heats of formation and molecular geometries that are greatly in error. Moreover it seems to be particularly unsatisfactory in the case of unusual ("nonclassical") structures; thus cyclopropanone (**5**) was predicted[8]

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[1] Part XV: M. J. S. Dewar and M. C. Kohn, *J. Amer. Chem. Soc.*, **94**, 2699 (1972).

[2] This work was supported by the Air Force Office of Scientific Research through Contract F44620-70-C-0121.

[3] M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Clarendon Press, Oxford, 1949.

[4] M. J. S. Dewar, *Nature (London)*, **156**, 789 (1945); *J. Chem. Soc.*, 406, 777 (1946); *Bull. Soc. Chim. Fr.*, C71, 18 (1951).

[5] F. W. Schneider and B. S. Rabinovitch, *J. Amer. Chem. Soc.*, 84, 4215 (1962).

[6] J. Casanova, Jr., N. D. Werner, and R. E. Schuster, *J. Org. Chem.*, 31, 3473 (1966).

[7] G. W. Van Dine and R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 3227 (1968).

[8] R. Hoffmann, *ibid.*, **90**, 1475 (1968).