EXTENDED HÜCKEL THEORY—V

CUMULENES, POLYENES, POLYACETYLENES AND C_n

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Abstract—Approximate calculations of the extended Hückel type are reported for ground and excited states of cumulenes, polyenes, polyacetylenes and C_n. Bond length variation in these molecules is studied by an iterative method which relates bond distance to Mulliken overlap population. For the cumulenes, simple anions and cations as well as the first excited state prefer some twisting of the terminal CH_2 groups from the ground state geometry. In the case of allene skeletal bending is also indicated in the excited state. An alternation of torsional barriers in the cumulene series is predicted. For the ground state of butadiene, one calculates a potential curve to twisting around the central single bond which has the *s-cis* form as a potential maximum, and which shows no activation energy to *cis-trans* interconversion. The first excited state of butadiene prefers a geometry with one CH_2 group twisted out of plane. Distinct *cis* and *trans* bending tendencies in various excited acetylene states are obtained. Bond alternation is found for polyacetylenes, polyenes, essentially none for cumulenes. For linear C_n an intermediate situation occurs; bond alternation appears in short chains, is not expected to persist for large n, but a large "end effect" is predicted. C_n rings with $n = 4q + 2$ become more stable than the corresponding linear chains for $n \geq 10$.

THE cumulenes, C_nH_4, are a group of molecules with cumulated double bonds, the first and best known members of the series being ethylene and allene.

$$H_2C{=}CH_2 \qquad H_2C{=}C{=}CH_2$$

Higher members of the group, with n = 4,5,6,8,10 are known, largely through the work of Kuhn.[2] Probably their most interesting feature, both for the experimental and theoretical organic chemist, is their ground state geometry, being planar for n even, and thus permitting geometrical isomerism in substituted derivatives, perpendicular (with respect to the terminal CH_2 groups) for n odd, and thus allowing optical isomerism.[3] This isomerism was of course predicted by van't Hoff[4] and rephrased in quantum mechanical language more recently.[5,6] The excited states of these molecules are also of interest in connection with the thermal and photochemical interconversion of substituted isomers.[7] Theoretical considerations by Mulliken[8,9] led to the conclusion

[1] Work performed while the author was a Junior Fellow, Society of Fellows, Harvard University.

[2] Some recent reviews are: [a] P. Cadiot, W. Chodkiewicz, and J. Rauss–Godineau, *Bull. Soc. Chim. Fr.* 2176 (1961); [b] H. Fischer in *The Alkenes* (Edited by S. Patai) p. 1025 Interscience, New York, (1964).

[3] The first resolution of an optically active allene derivative was made by P. Maitland and W. H. Mills, *Nature, Lond.* **135**, 994 (1935); *J. Chem. Soc.* 987 (1936).

[4] J. van't Hoff, *La Chimie dans L'Espace*, Paris (1875); *The Arrangement of Atoms in Space* (2nd Edition) p. 103. Longmans Green, London (1898).

[5] F. Seel, *Z. Phys. Chem.* **B53**, 103 (1943).

[6] B. Pullman and G. Berthier, *Bull. Soc. Chim. Fr.* **16**, 145 (1949).

[7] G. S. Hammond and N. J. Turro, *Science*, **142**, 1541 (1963) and Ref. therein.

[8] R. S. Mulliken and C. C. J. Roothaan, *Chem. Revs.* **41**, 219 (1947).

[9] R. S. Mulliken, *Tetrahedron* **5**, 253 (1959).

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that the first few excited states of ethylene prefer a perpendicular conformation; it has also been suggested that further distortion from local planarity at each carbon takes place.[10] The spectral evidence indicates only that the excited molecule is nonplanar.[8-11] Some calculations on $C_2H_4^+$ yield a potential energy curve for rotation about the C=C bond which has a shallow minimum for a slightly twisted form, with a larger barrier at the perpendicular geometry[9] (but smaller in magnitude than for ethylene itself). There have also been some experimental studies on negative ions: mono- and di-negative ions of some higher n-even cumulenes have been synthesized and their electronic absorption spectra studied;[12,13] the ESR spectrum of $C_2H_4^-$ has recently been recorded.[14] Finally, precise structural studies are available for compounds with n = 2,[15] 3,[16,17] 4,[18,19] and in the case of butatriene there appears a significant difference between the terminal and central bond lengths.[20] In this work the study of the detailed geometries of these molecules, their excited states and ions is extended.

The polyacetylenes, C_nH_2, n even, possess a series of alternating single and triple bonds. Best known are acetylene and diacetylene.

$$HC\equiv CH \qquad HC\equiv C—C\equiv CH$$

Structural studies are available for n = 2,[21] 4,[21] 6.[22] On the theoretical side the persistence of bond alternation for large n has been investigated.[23] The first excited state of acetylene has a longer C—C bond than the ground state, and is not linear, but *trans* bent.[24,25]

The series of molecules C_n has not been accessible by ordinary synthetic techniques, but rather consists of species detectable only at very high temperatures, particularly in association with graphite. Relative abundances for C_n obtained by various techniques are available, but it is often not clear in the experiments to what extent equilibrium was attained. These molecules have been studied theoretically by Pitzer *et al.*[26,27] who also review critically the experimental situation. The calculations described here

[10] A. D. Walsh, *J. Chem. Soc.* 2325 (1953).

[11] P. G. Wilkinson and R. S. Mulliken, *J. Chem. Phys.* **23**, 1895 (1953).

[12] G. Hoijtink and P. H. van der Meij, *Z. Phys. Chem. Frankfurt*, **20**, 1 (1959).

[13] A. Zweig and A. K. Hoffmann, *J. Amer. Chem. Soc.* **84**, 3278 (1962).

[14] K. W. Bowers and F. D. Greene, private communication.

[15] J. M. Dowling and B. P. Stoicheff, *Canad. J. Phys.* **37**, 703 (1959).

[16] B. P. Stoicheff, *Canad. J. Phys.* **33**, 811 (1955).

[17] A. Almenningen, O. Bastiansen, and M. Traetteberg, *Acta. Chem. Scand.* **13**, 1699 (1959).

[18] B. P. Stoicheff, *Canad. J. Phys.* **35**, 837 (1957).

[19] Unpublished work by A. Almenningen, O. Bastiansen and M. Traetteberg, quoted by O. Bastiansen and M. Traetteberg, *Tetrahedron* **17**, 147 (1962).

[20] M. M. Woolfson, *Acta. Cryst.* **6**, 838, (1953), studied tetraphenylhexapentaene, *assumed* equal bond lengths in the cumulene chain, obtaining an average C=C distance of 1·31 ± 0·03 Å.

[21] J. H. Callomon and B. P. Stoicheff, *Canad. J. Phys.* **35**, 373 (1957).

[22] G. A. Jeffrey and J. S. Rollett, *Proc. Roy. Soc.* A213, 86 (1952).

[23] H. C. Longuet–Higgins and F. H. Burkitt, *Trans. Far. Soc.* **48**, 1072 (1952).

[24] C. K. Ingold and G. W. King, *J. Chem. Soc.* 2702, 2708 (1953).

[25] K. K. Innes, *J. Chem. Phys.* **22**, 863 (1954).

[26] K. S. Pitzer and E. Clementi, *J. Amer. Chem. Soc.* **81**, 4477 (1959).

[27] S. J. Strickler and K. S. Pitzer in *Molecular Orbitals in Chemistry, Physics and Biology* (Edited by P.—O. Löwdin and B. Pullman) Academic Press, New York (1964).

may shed some light on the extent to which C_n may be represented by the valence structure shown below.

$$:C{=}C{=}(C{=}C)_x{=}C{=}C:$$
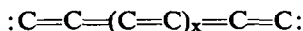
The polyenes, $CH_2{=}CH({-}CH{=}CH)_x{-}CH{=}CH_2$ have been the subjects of numerous theoretical studies concerned with their spectra, the predicted persistence of bond alternation,[28] and the form of the potential surface for twisting around the formal single bonds. The main concern in this work will be with the latter point, and with the geometrical changes upon electronic excitation in these molecules.

The method of calculation is the extended Hückel theory. This is a one-electron, semiempirical, MO method which, it is claimed, allows one to make a rough, internally consistent, guess at the electronic structure of all molecules, organic and inorganic, conjugated and unconjugated.[29] It can be viewed both as a simple extension of Hückel π-electron theory to include σ-electrons, or as a formalization of the very successful MO arguments that Walsh has used for smaller molecules.[30]

Large and fast computers have allowed one to treat a great number of realistic molecules in a relatively short time, and have shown that the semiempirical model is fairly successful in accounting for the geometries, qualitative charge distributions, and relative stabilities of molecules in their ground, and sometimes, excited states. Some serious and anomalous failures make it clear that the most reliable results are produced when a large series of related molecules containing four to fifteen atoms is studies, and where one can make a comparison with experimental reality for part of the series. Energy differences quoted in this paper are not to be taken literally, but must be weighed relative to similar computed quantities.

As an MO theory with an atomic orbital basis, the extended Hückel theory does not immediately yield bonds, nor does it give a separation of the total molecular energy into components, such as electronic, steric, etc. The supplementary population analysis[31,32] tries to abstract the essential features of the electronic distribution, and allows one to argue from bonding (overlap populations) and charge distributions. Still no way is available to separate the energy into components such as most chemists would like to have. Nevertheless both electronic and steric, bonded and nonbonded contributions are definitely involved. The presence of an electronic factor may be inferred, for example, from the correctly calculated geometries of the series: FCCF (linear), FNNF (bent planar, *cis* and *trans* isomers, *cis* more stable), FOOF (bent nonplanar); the change in geometry in the first excited state of ethylene; the falloff in the ionization potential of the alkanes with increasing chain length; the stabilization of nonclassical carbonium ions. That a steric factor is present is probably best seen when one performs a calculation on the ground state of two neutral molecules, such as ethylenes, brought close to each other. With decreasing separation the energy of the total system rises very steeply—repulsion—to fall again as new bonds are formed

[28] H. C. Longuet–Higgins and L. Salem, *Proc. Roy. Soc.* A251, 172 (1958), *Ibid.* A257, 445 (1960).

[29] R. Hoffmann: I. *J. Chem. Phys.* 39, 1397 (1963); II. *Ibid,* 40, 2745 (1964); III. *Ibid.* 40, 2474 (1964); IV. *Ibid.* 40, 2480 (1964); see also *J. Chem. Phys.* 40, 2047 (1964); *J. Amer. Chem. Soc.* 86, 1259 (1964).

[30] A. D. Walsh, *J. Chem. Soc.* 2260, 2266, 2288, 2296, 2301, 2306, 2318, 2321, 2325, 2330 (1953).

[31] R. S. Mulliken, *J. Chem. Phys.* 23, 1833, 1841, 2338, 2343 (1955).

[32] See C. W. Kern and M. Karplus, *J. Chem. Phys.* 40, 1374 (1964); for deficiencies in such analysis.

to yield cyclobutane. In this paper a study is presented of the ground and excited states of some molecules for which both steric and electronic factors are important. Butadiene is such a molecule; it is also the prototype of the conjugated polyenes, a group of molecules of primary interest in organic photochemistry.[7,33] The latter area will be discussed in detail in subsequent work.

The parameters used for C and H are identical to those used previously for hydrocarbons.[29,33a] The problem of the variation in bond lengths was attacked in the following iterative manner. From the previous work[29] total C—C overlap populations were available for acetylene, ethylene, benzene and ethane, computed at distances of 1·21, 1·34, 1·40, 1·54 Å respectively. The best empirical total $(\sigma + \pi)$ overlap population vs. bond distance curve which passed through these points was fitted. The expression used was a quadratic

$$r = 1\cdot860297 - 0\cdot548695n + 0\cdot109747n^2 \tag{1}$$

where n is the overlap population, r the C—C distance. Assuming some starting r, a calculation was carried out, obtaining the populations n. From these new distances were computed by the above prescription and the process continued until approximate self-consistency was obtained. Two reservations with respect to this procedure should be pointed out. First, granting a correlation between bond orders or overlap populations and bond distances, there is no reason to assume that only a single relationship exists for all bonds,[34] for instance that one and the same curve holds for saturated and olefinic bonds. Secondly, the choice of total $\sigma + \pi$ overlap population cannot be rationalized—it was, however, the only choice available in view of the absence of a $\sigma - \pi$ separation in the nonplanar cumulenes. It should also be remarked that, unlike the usual bond alternation theory,[28] the use of an empirical expression such as (1) does not guarantee that the energy will reach a minimum when self-consistency with respect to bond orders is attained. As a matter of fact the extended Hückel theory yields bad predictions of absolute C—C distances in ethane, ethylene and acetylene,[29] and predicts no minimum at all for C_2. In a sense the bond variation calculations are an attempt to overcome this failure of the theory, and as will be seen, they succeed partially. It should also be remarked that the method used in these calculations, like the ordinary Hückel theory, does not in the first approximation discriminate between states differing in spin multiplicity.

Cumulenes

For conformational studies the molecules C_nH_4, with n = 2–10 were assigned the initial model geometry with C=C 1·34 Å, C—H 1·10 Å. The motions or distortions examined were: simple twisting about the C_n axis; elongation or contraction of C=C bonds, distortions from local trigonal to tetrahedral symmetry at the terminal carbons, bending of the C_n skeleton from linearity. The symmetry designation of the calculated preferred geometries is given below; D_{2h} being planar as ethylene, D_{2d} perpendicular as allene, D_2 twisted through some angle θ, $0° < \theta < 90°$, C_2 twisted

[33] *Advances in Photochemistry* (Edited by W. A. Noyes, Jr., G. S. Hammond and J. N. Pitts, Jr.) Vol. I. Interscience, New York (1963);

[33a] The use of the same atomic parameters in a neutral molecule and its cation is a deficiency of these calculations.

[34] See the *Epistologue on Carbon Bonds* in *Tetrahedron* 17, 3 (1962).

and distorted from trigonal symmetry, as hydrazine, C_{2v} bent, nonlinear, but planar, C_1 bent and twisted.

	ethylene	allene
ground state	D_{2h}	D_{2d}
first excited ($\pi \to \pi^*$) state	D_{2d}	C_{2v}
+1 ion	D_2	D_2
+2 ion	D_{2d}	D_{2h}
−1 ion	D_2	D_2 or C_1
−2 ion	D_{2d} or C_2	C_{2v}

FIG. 1. Variation of energy with angle of simple twisting for ethylene and allene. 0, *, +1, +2, −1, −2 refer to ground state, first excited state, +1, +2, −1, −2, ions respectively. Arbitrary energy zero for a planar molecule for all states. For all states these calculations were done for the same C=C distance of 1·34 Å.
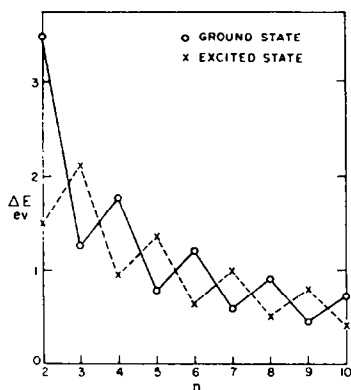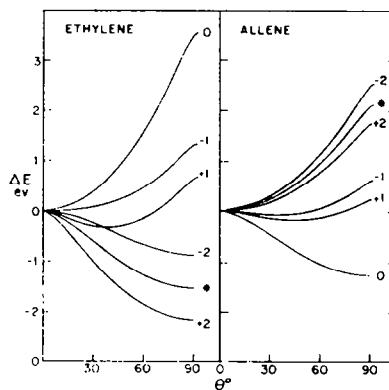

FIG. 2. n Dependence of torsional barrier in ground and excited states.

The skeletal bending distortion for allene was suggested by Walsh.[35,36] The calculated bending in excited allene is to a CCC angle of 165°, and the minimum is shallow. In the negative ion the bending is very slight (~170°), and in the dianion pronounced (~130°). Various combinations of bending motions were found to be unfavourable for butatriene ions and excited states, so that it seems likely that all n even cumulenes will behave as ethylene. For the simple twisting the specific variation of energy with angle of twist is shown for ethylene and allene in Fig. 1. Figure 2 illustrates the n dependence of the energy difference by which the ground state prefers to be planar (n even) or perpendicular (n odd), and the excited state prefers to be perpendicular

[35] A. D. Walsh, J. Chem. Soc. 2266 (1953).
[36] L. H. Sutcliffe and A. D. Walsh, J. Chem. Soc. 849 (1952).

(n even) or planar (n odd). For the n odd cumulenes the bending is not included. The odd-even difference, the tendency of excited n odd states to fall on the ground n even curve, and the converse, should be noted. The energy differences vary linearly with $1/n$ for larger n and extrapolate to zero as $n \rightarrow \infty$.[37] The general features of the curves for the ground, excited states and cation of ethylene agree well with the calculations presented by Mulliken.[8] The best experimental estimate of the $D_{2d} - D_{2h}$ difference in ground state ethylene comes from the energy of activation to thermal *cis-trans* isomerization in dideuteroethylene, and is 2·8 ev.[39] The calculated energy difference with C=C at 1·34 Å in both geometries is 3·5 ev. As the molecule twists from planarity, there will also take place an elongation of the C=C bond. The bond variation method gives an equilibrium distance for D_{2d} ethylene of 1·46 Å.[40] Comparing D_{2h} at 1·34 Å with D_{2d} at 1·46 Å, the energy difference decreases to 3·0 ev. Since the calculations are approximate it can only be concluded that the calculated torsional barrier is not unreasonable.

The calculated barrier in allene appears low.[41] It would be interesting to have available detailed studies of the thermal and photochemical racemization of optically active allenes.[42] Unlike the case of ethylene, no orbital degeneracy intervenes at 90° twist from the ground state conformation, and it may be that in the case of allene the triplet excited state will not dip below the twisted ground state (for a planar allene the calculated ground state is 1·7 ev below the excited state). *Cis-trans* isomerism has been studied in the substituted butatrienes,[43-45] and an energy of activation of 0·85 ev has been reported for one derivative.[43,46] Geometric isomers of higher cumulenes are apparently easily interconvertible.

In the ions the energy differences between potential extremes also decrease with n. For ethylene the minima in the +1 and −1 ion curves occur at angles of 35° and 1°

[37] J. D. Dunitz and L. E. Orgel, *J. Chem. Phys.* **20**, 1328 (1952) also concluded that the energy difference will tend to zero with increasing n; but they found no odd-even alternation in the torsional barrier. See also E. M. Shustorovich, *Zh. Strukt. Khim.* **4**, 642, 793 (1963); **5**, 327 (1964);

M. V. Volkenshtein, *Configurational Statistics of Polymer Chains* p. 66. Moscow, USSR Academy of Sciences (1959) lists some torsional barriers for ethylene (39·3 kcal/mole) and allene (27·2) based on torsional frequencies, but these appear low. Also given are barriers for cumulenes with n = 4 (19·0), n = 5 (14·0), n = 13 (5·3), quoted from A. Lösche, *Kerninduktion*. Berlin (1957). The lack of the latter source has prevented a detailed examination of these values—but there appear to be no syntheses of $n = 13$ cumulenes in the literature, and pentatetraenes have been synthesized only very recently.[38]

[38] R. Kuhn, H. Fischer and O. Fischer, *Chem. Ber.* **97**, 1760 (1964).

[39] J. E. Douglas, B. S. Rabinovitch and F. S. Looney, *J. Chem. Phys.* **23**, 2439 (1955).

[40] This is also the calculated equilibrium distance in the first excited state of ethylene. In Ref. 11 it is concluded that the planar ethylene V state has an equilibrium distance of 1·69 Å; the twisted excited state would have a shorter C=C bond.

[41] The ratio of ethylene to allene barriers is very similar to an extrapolation of the twisting frequency calculations of R. G. Parr and G. R. Taylor, *J. Chem. Phys.* **19**, 497 (1951).

[42] Refs to resolutions of optically active allenes may be found in the recent review by A. A. Petrov and A. V. Fedorova, *Usp. Khim.* **33**, 3 (1964). It appears that the resistance to thermal racemization has been studied only along with the first such synthesis.[a]

[43] R. Kuhn and K. L. Scholler, *Chem. Ber.* **87**, 598 (1954).

[44] R. Kuhn and D. Blum, *Chem. Ber.* **92**, 1483 (1959).

[45] W. Jasiobedzki, *Roczn. Chem.* **33**, 321 (1959).

[46] However, in the same work[45] the ethylene analogue was reported to have a similar activation energy, which would be surprisingly small.

respectively, for allene at 45° and 30° from planarity. For the same ions in $C_{10}H_4$ and C_9H_4 the minima are approximately 35° and 25°. The bond distance variation for all states was studied extensively only for ethylene and allene. Qualitatively the following order of C=C distances in various states of ethylene was obtained.

$$+2 < \text{ground} < +1 < \text{first excited} < -1 < -2$$

For linear allene the order is similar except that the ground state and $+1$ distances come out nearly the same. The calculations are not considered sufficiently reliable to decide if both C=C bonds are of equal length in excited allene.
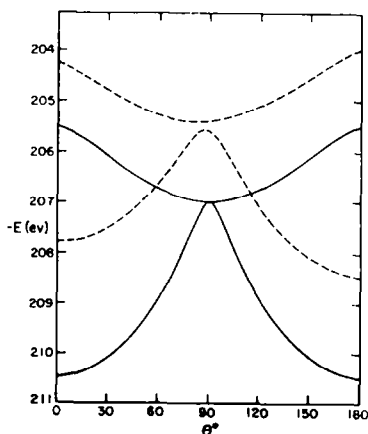

FIG. 3. Energy variation with angle of twist for trigonal (solid line) and tetrahedral (dashed line) ethylene, both at C=C 1·34 Å. The lower curve of each set is the ground state, the upper the first excited state. For the tetrahedral ethylene, 0° twist corresponds to eclipsing "holes"

The suggestion of Walsh[10] that there is a combination of twisting and distortion from near trigonal local symmetry in excited ethylene was investigated in some detail, but unfortunately the number of degrees of freedom in the combined motions of stretching, twisting, bending and distortion is so great and the theory so approximate that the results are considered to be somewhat ambiguous. For the ground, first excited states, $+1$, $+2$, -1 ions of ethylene the distortion is not favored according to these calculations.[47] For the -2 ion, which is isoelectronic with hydrazine, the calculations show virtually identical energies for trigonal and tetrahedral forms, both best twisted about 90°. For this reason the noncommital entry "D_{2d} or C_2" appears in the list above. The calculations appear to be less ambiguous for the allene -2 ion, showing only strong CCC bending and a planar molecule. The rotational dependence of the energy of the tetrahedrally distorted ethylene is interesting, and is shown in Fig. 3 for the ground and first excited states. It will be noticed that while the tetrahedral curve is always at higher energy than the trigonal, there are some points on the former curve which are at lower energy than the most unstable (near 90°) trigonal

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[47] L. Burnelle (private communication) has performed some calculations which do suggest tetrahedral distortion in the first excited state.

ethylene. These distorted forms are, however, inaccessible by simple bending back of hydrogens. Note also the asymmetry of the tetrahedral curve.

Figure 4 shows the energy of the highest occupied and lowest unoccupied molecular orbitals as a function of n, in the favored linear geometry. The gap between these levels is consistently greater for n odd, and extrapolates to zero with increasing n. Spectral predictions from simple theories are notoriously bad, but there is qualitative agreement here in that allene absorbs at higher energy than ethylene,[48] pentatetraenes absorb at higher energies than butatrienes[38] and for n-even cumulenes there is the anticipated uniform red shift with increasing n.[49,50] As far as the spectra of the
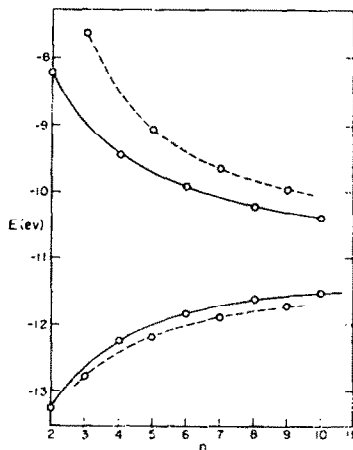

Fig. 4. Calculated energies of highest occupied and lowest
unoccupied molecular orbitals in the cumulenes. Solid line
joins points for n even, dashed line for n odd.

anions are concerned, Zweig and Hoffmann[13] have already on the basis of Hückel calculations concluded that the −2 and probably −1 ion of tetraphenylbutatriene is nonplanar. The change in geometry is of course important in attempts to calculate the spectra.

In previous work the detailed ethylene wave function was presented as well as the results of a population analysis for ethylene and allene.[29] Some net charges and overlap populations for D_{2d} C_9H_4 and D_{2h} $C_{10}H_4$ are shown in Table 1. There is some variation along the chain. It appears that overlap populations and charges will converge to a limiting value in the interior of a long chain. The populations were used in the iterative bond length variation process described above. For allene, butatriene, C_9H_4 and $C_{10}H_4$ the final distances, converged to ± 0.005 Å, are listed in Table 2. The experimental values are 1·309 for allene,[16,17] 1·318, 1·284 for butatriene.[19] Agreement is poor for the butatriene 1–2 bond, better than some previous theoretical work;[23] worse than other.[51] It appears that all interior bonds in C_nH_4 will be shorter than in ethylene, as already concluded by Pullman and Berthier,[6,52] among the interior bonds the variation will be small, alternating and nonpersistent.

[48] L. H. Sutcliffe and A. D. Walsh, J. Chem. Phys. 19, 1210 (1951).
[49] H. Krausch, J. Chem. Phys. 28, 898 (1958).
[50] F. Bohlmann and K. Kieslich, Chem. Ber. 87, 1363 (1954).
[51] A. Julg and A. Pellégatti, Theoretica. Chimica. Acta 2, 396 (1964).
[52] A similar conclusion is obvious from simple hybridization arguments.

TABLE 1. NET CHARGES AND OVERLAP POPULATIONS FOR NONAOCTAENE AND DECANONAENE

Atom	Q(i)		Bond	n(i,j)	
	C_9H_4	$C_{10}H_4$		C_9H_4	$C_{10}H_4$
1	−0·270	−0·216	1–2	1·2769	1·2705
2	+0·145	+0·089	2–3	1·3614	1·3689
3	−0·170	−0·109	3–4	1·3330	1·3226
4	+0·063	−0·008	4–5	1·3409	1·3496
5	−0·134	−0·048	5–6		1·3272

TABLE 2. FINAL DISTANCES FROM THE BOND VARIATION PROCESS FOR CUMULENES

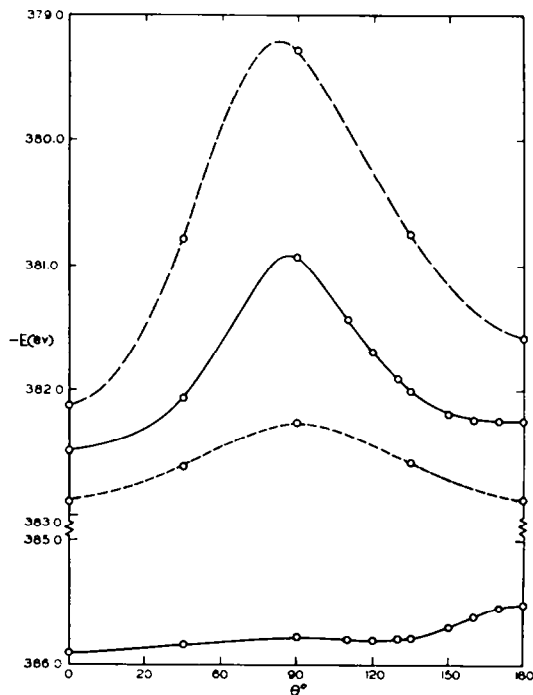| Bond	C_3H_4	C_4H_4	C_9H_4	$C_{10}H_4$
1–2	1·320	1·346	1·342	1·346
2–3		1·284	1·304	1·298
3–4			1·321	1·330
4–5			1·314	1·305
5–6				1·328

FIG. 5. Potential curve for twisting around the central single bond in butadiene: ——— planar ground and excited state, − − − − "twist one" (see text), — — — "twist both". 0° is the *s-trans*, 180° the *s-cis* form.

Butadiene

The model geometry used had C=C 1·34 Å, C—C 1·48 Å, C—H 1·10 Å, angles all 120°—a slight idealization of the experimental values.[53,54] In Fig. 5 is shown the potential curve for rotation about the central single bond for the ground state, planar $\pi^* \leftarrow \pi$ excited state, excited state with one =CH$_2$ group twisted 90° out of the plane ("twist one"), excited state with both =CH$_2$ groups twisted 90° from planarity ("twist both"). In the ground state the following should be noted: (1) The *s-trans* form is calculated to be more stable than the *s-cis* by 0·413 ev = 9·53 kcal, of which 1·75 is in the π orbitals, 7·78 in the σ framework. (2) There is no activation energy in going from *s-trans* to *s-cis*. (3) The *s-cis* form is not a local minimum, but a metastable maximum of the energy surface. The peculiar shape of the potential surface, the $\sigma-\pi$ decomposition of the *s-cis–s-trans* energy difference, the slightly more positive character of the hydrogens which approach most closely in the *s-cis* form can be verbally rationalized by predicating steric repulsion in the *s-cis* conformation, superimposed onto an electronic energy which already favors the *s-trans* form by a little.

There have been a number of studies of chemical, structural, spectroscopic and thermodynamic properties of butadiene[55–65] or its derivatives[66–76] in which the question of the potential energy surface with respect to rotation about the central single bond in the ground state has come up. The relative merits of the various arguments will not be reviewed here.[77] The consensus of opinion appears to be that while structural determinations[53,54] reveal only the *s-trans* geometry, free butadiene also exists in the

[53] A. Almenningen, O. Bastiansen and M. Traetteberg, *Acta. Chim. Scand.* **12**, 1221 (1958).
[54] D. J. Marais, N. Sheppard and B. P. Stoicheff, *Tetrahedron* **17**, 163 (1962).
[55] V. Schomaker and L. Pauling, *J. Amer. Chem. Soc.* **61**, 1769 (1939).
[56] R. S. Mulliken, *J. Chem. Phys.* **7**, 121 (1939).
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[67] G. J. Szasz and N. Sheppard, *Trans. Far. Soc.* **49**, 358 (1953).
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s-cis form to the extent of a few percent.[78] The *s-cis* form is encountered in transition metal complexes[79] and there is a massive accumulation of evidence that in some organic reactions (eg. the Diels-Alder reaction) the transition state involves an *s-cis* diene, and that the energy of activation for the *trans-cis* interconversion must be small. In my opinion there has been no unambiguous direct physical measurement on free *s-cis* butadiene.[80]

The lack of an energy of activation to the *cis-trans* isomerization in the calculated potential curve, and the related potential instability of the strictly *s-cis* form appear to be in disagreement with generally accepted notions; the *cis-trans* energy difference is also too large.[81] As was mentioned above, these calculations are unreliable as far as absolute energies are concerned, and it could be that the overestimation of steric effects noted in previous work by the same method[29] could be responsible for the excessive destabilization of the *s-cis* butadiene. However, it is felt that in view of the inconclusive experimental evidence one cannot reject the calculated curve.

Fateley *et al.*[76] have recently presented a very interesting analysis of $=C-C=$ torsions. If one retains the first three terms of a Fourier expansion of the potential hindering the internal rotation, i.e.

$$V(\alpha) = \frac{V_1}{2}(1 - \cos \alpha) + \frac{V_2}{2}(1 - \cos 2\alpha) + \frac{V_3}{2}(1 - \cos 3\alpha)$$

then the calculated ground state butadiene curve resembles in shape a hypothetical curve with V_1, V_2, V_3 of comparable magnitude. In fact only a poor fit can be obtained from the above expression with a largest V_1, smaller V_2 and V_3, and V_2 negative. Again a sharply rising nonbonded repulsion at the *cis*-geometry is implicated.

The theoretical situation is not clear. There have been numerous π-electron calculations on butadiene,[82–84] and most of those which compare *s-cis* and *s-trans* conformations find the *s-cis* form more stable. A more complete recent calculation by I. Fischer-Hjalmars[85] considers the effects of conjugation and nonbonded repulsions in *s-cis*, *s-trans*, and a conformation rotated 90° around the single bond. This shows *s-trans* more stable than *s-cis* by 5·9–8·1 kcal/mole, with the 90° form 4·4–1·9 kcal/mole above the energy of the *s-cis* geometry. The calculated potential curve differs in shape from that computed here by the presence of a potential hill at intermediate angles of twist.

Allinger and Miller[86] have recently reported a Pariser-Parr calculation on the ground and excited states of butadienes as a function of twisting. These calculations apparently yield a potential curve similar to that of Fischer-Hjalmars, and are in

[78] The possibility of an energy maximum at the *s-cis* form is also mentioned by E. L. Eliel, *Stereochemistry of Carbon Compounds* p. 331. McGraw Hill, New York (1962). See also Ref. 76.

[79] eg. O. S. Mills and G. Robinson *Acta. Cryst.* **16**, 758 (1963).

[80] See, however, Refs 59, 62.

[81] The observed torsional fundamental of 163 cm⁻¹, R. K. Harris, *Spectrochim. Acta* **20**, 1129 (1964), also implies a considerably steeper rise of the potential curve in the vicinity of the *s-trans* form than that calculated.

[82] R. G. Parr and R. S. Mulliken, *J. Chem. Phys.* **18**, 1338 (1950).

[83] R. S. Berry, *J. Chem. Phys.* **26**, 1660 (1957) and Refs therein to previous work.

[84] O. Sovers and W. Kauzmann, *J. Chem. Phys.* **38**, 813 (1963).

[85] I. Fischer–Hjalmars, *Tetrahedron* **19**, 1805 (1963).

[86] N. L. Allinger and M. A. Miller, *J. Amer. Chem. Soc.* **86**, 2811 (1964).

good agreement with the experimentallly observed energy of the diene $N \rightarrow V_1$ transition. Qualitatively similar behavior for transition to the first excited state is seen in Fig. 5, but again one must say that useful absolute spectral predictions cannot be expected of the extended Hückel method.

The one-electron calculation on the excited state (multiplicity unspecified) show the following features: (1) In its first excited state butadiene apparently prefers to have one methylene group twisted 90° from coplanarity with the rest of the molecule. This geometry is better than that with the molecule remaining planar, which in turn is preferred to "twist both".[87] (2) In all excited state conformations a considerable potential hill appears at intermediate angles of twist; it is largest in "twist both", smallest in "twist one". The s-trans form is favored in the "twist one" excited state by only 0·4 kcal/mole. At 90° there are several excited state configurations of similar energy. (3) The vertical transition to the excited state is shifted to greater energy for intermediate angles of twist.[86]

Now while the geometry of the excited state has not been treated theoretically,[88] simple orbital or resonance arguments lead to qualitative conclusions very similar to those presented here. In MO language, the first excited state involves promotion of an electron which is originally in an orbital antibonding with respect to the 2–3 bond, to an orbital which is bonding in that region. In valence bond language there is a large contribution in the excited state from resonance structures with a central double bond. In either case the increased double bond character of the central bond can be interpreted as leading to a greater restriction of free rotation around that bond. Corresponding decrease in double bond character of the terminal bonds coupled with the established stabilization of an allylic fragment make reasonable an excited state twisted around a single terminal bond.

These conclusions are in agreement with the photochemical evidence on the isomerization of substituted butadienes.[89–92] Spectroscopic studies of the $N \rightarrow V_1$ transition,[57,58] have apparently not detected nor considered any possible geometry change in the excited state. The spectroscopic consequences of partial twisting in cyclic dienes are well treated in the work of Allinger and Miller.[86]

The calculations may also be applied to the simple anions and cations of butadiene. It is found that $C_4H_6^-$ prefers a planar geometry,[93] $C_4H_6^+$ wants to twist slightly both or one of the terminal bonds,[94] $C_4H_6^{+2}$ would rather be twisted around one

[87] Twisting one $=CH_2$ group through 90° is better than twisting both through some smaller angle. An accompanying distortion from trigonal symmetry, as suggested by Walsh for ethylene[10] was not studied. In all the calculations in this paper the bond lengths in the excited butadiene were kept at the ground state values. No doubt these change in the excited state in the direction of shortening the central bond and lengthening the terminal bonds.

[88] R. S. Mulliken, Rev. Mod. Phys. 14, 260 (1942) discussed it briefly, concluding that it might retain planarity.

[89] R. Srinivasan, J. Amer. Chem. Soc. 84, 4141 (1962).

[90] G. S. Hammond, N. J. Turro and P. A. Leermakers, J. Phys. Chem. 66, 1144 (1962).

[91] G. S. Hammond and R. S. H. Liu, J. Amer. Chem. Soc. 85, 477 (1963).

[92] G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt and C. Dalton, J. Amer. Chem. Soc. 86, 3197 (1964).

[93] The esr spectrum of $C_4H_6^-$ has been observed by D. H. Levy and R. J. Myers, J. Chem. Phys. 41, 1062 (1964). Only two distinct proton couplings are observed.

[94] D. A. Hutchinson, Trans. Far. Soc. 59, 1695 (1963) has also examined $C_4H_6^+$ theoretically and found no tendency for distortion from a symmetrical structure.

terminal bond, while $C_4H_6^{-2}$ is a borderline case, with slight preference for a planar over a singly twisted molecule. Some calculated energies (relative to the most stable *s-trans* form) are shown below for butadiene anions and cations, in the planar geometry.

	90°	*s-cis*
+2	0·736 ev	0·281 ev
+1	0·440	0·357
−1	1·250	0·302
−2	2·356	0·191

Again the relative trend to a larger barrier to interconversion and smaller *cis-trans* difference with increasing positive or negative charge could have been anticipated from simple arguments. Though it would be dangerous to extrapolate these calculations to more extended conjugated systems such as the cyano derivatives of butadiene, it is interesting that in a recent study of hexacyanobutadiene and its anions[95] it was possible to separate two interconvertible isomers, presumably *s-cis* and *s-trans*, of the dianion. An estimate of the *cis-trans* energy difference given is 0·8 kcal/mole, certainly less than a comparable value for neutral butadiene. The equilibrium geometry must be quite abnormal if a truly planar *s-cis* form is to be accommodated, and it may be that the molecule twists around a terminal bond.

Some preliminary work was done on the higher polyenes. For *trans*-1,3,5-hexatriene all possible combinations of simple twists around double bonds were studied in excited states and ions. In the first excited state and the +2 ion, the hexatriene preferred a conformation twisted 90° around the *central* double bond to a planar one, or to one twisted around the terminal bond, thus testifying again to the stability of the allylic fragment. The +1, −1, −2 ions preferred planar conformations, but partially twisted forms were not studied. A similar study for *trans-trans*-1,3,5,7-octatetraene finds a preference for retention of planarity in the first excited state. Presumably all higher polyenes will also remain planar. It may be difficult to compare these calculations to the results of photochemical isomerization experiments, since even when a polyene such as octatetraene remains planar in the excited state, the torsional barriers about all double bonds are lowered. A calculation on the polyene $C_{12}H_{14}$ showed the persistence of bond alternation with extrapolated distances in the interior of a long polyene of C═C 1·37, C—C 1·43 Å.[28,96] The bond variation method gives a poor 1·45 Å (observed 1·48[53,54]) for the central butadiene bond.

A calculation was also carried out on divinyl acetylene (1,5-hexadiene-3-yne) to study conformational isomerism about a triple bond and two adjacent single bonds. Pauling,[97] on the basis of the bent bond picture of multiple bonding concludes that the *cis* configuration should be the most stable by about 0·4 kcal. The calculations here give the *trans* form more stable by 0·02 kcal/mole than the *cis*, with a 90° twisted form 0·15 kcal/mole above the latter. The experimental evidence does not relate directly to this molecule and is discussed by Pauling.[97-99]

[95] O. W. Webster, *J. Amer. Chem. Soc.* **86**, 2898 (1964).

[96] Y. Ooshika, *J. Phys. Soc., Japan*, **12**, 1238, 1246 (1957).

[97] L. Pauling, *The Nature of the Chemical Bond* (3rd edition) p. 292, Cornell University Press, Ithaca, New York (1960).

[98] M. I. Batuev, A. P. Meshcheryakov and A. D. Matveeva, *Izv. Akad. Nauk. SSSR* 1485 (1959).

[99] A. A. Petrov, V. B. Lebedev and Yu. I. Porfir'eva, *Zh. Obshch. Khim.* **33**, 416 (1963).

Polyacetylenes

The molecules studied were C_nH_2, n = 2–16, n even, with $C\equiv C$ 1·20, C—C 1·40 Å. Bond variation calculations were done on C_4H_2, C_6H_2 and $C_{16}H_2$. In general there is little that is unusual in the polyacetylenes: charges and overlap populations (for a given type of bond) varied very little in the chain interior, as may be seen for $C_{16}H_2$ in Table 3. This is also reflected in the results of the bond variation procedure, which yields the following distances:

C_4H_2: 1·223, 1·434
C_6H_2: 1·226, 1·424, 1·240
$C_{16}H_2$: 1·227, 1·418, 1·246, 1·403, 1·252, 1·398, 1·253, 1·397

Experimental values are:

C_4H_2[21]: 1·205, 1·376
C_6H_2[22]: 1·20, 1·38, 1·20

While in this case we obtain poorer agreement with experimental distances than Longuet-Higgins and Burkitt,[23] there is the common conclusion that bond alternation will persist,[100] and that bond variation will be small. It might be added that $C_{16}H_2$

TABLE 3. OVERLAP POPULATIONS AND CHARGES FOR $C_{16}H_2$

Atom	Charge	Bond	n(i–j)
1	−0·210	1–2	1·8571
2	+0·039	2–3	1·0096
3	−0·003	3–4	1·7764
4	+0·013	4–5	1·0292
5	−0·001	5–6	1·7642
6	+0·005	6–7	1·0326
7	+0·001	7–8	1·7612
8	+0·002	8–9	1·0344

was used for a test of the convergence of the bond variation method by approaching self-consistency from two directions: from one initial calculation with the distances mentioned above, and also from another, with all the distances in the carbon chain set equal to 1·30 Å. The same final dimensions were obtained, though naturally the convergence from the second set was slower.

The lowest observed excited state of acetylene is ^1A_u, *trans* bent, with an estimated C—C bond length of 1·38 Å, and an HCC angle of 120°.[24] The electronic structure of acetylene has been discussed by several authors.[24,25,30,101–103] As a consequence of the C_{2h} (*trans*) or C_{2v} (*cis*) distortion the bonding acetylene π_u level splits into $a_u + b_u(b_1 + a_1)$, the antibonding π_g goes over to $a_g + b_g(b_2 + a_2)$. The b_g and a_u levels are antisymmetric with respect to the plane in which bending takes place, and thus are not much affected by the motion. According to Walsh[30] the $a_g(b_2)$ level is greatly

[100] E. M. Shustorovich and N. A. Popov, *Zh. Strukt. Khim.* **5**, 770 (1964) appear to disagree on this point. See also E. M. Shustorovich, *Ibid.* **6**, 123 (1965).
[101] R. S. Mulliken, *Canad. J. Chem.* **36**, 10 (1958).
[102] H. Howard and G. W. King, *Canad. J. Chem.* **37**, 700 (1959). The group theoretical notation in that paper differs slightly from that of Ref. 101,30 and this work. To compare, switch subscripts of B_1 and B_2 representations.
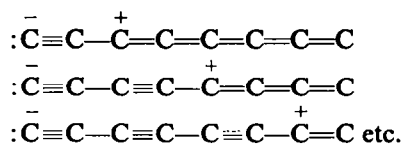[103] L. Burnelle, *J. Chem. Phys.* **36**, 2824 (1962).

stabilized by the bending, while the $b_u(a_1)$ level is somewhat destabilized. The calculations reported here agree with the former point, but disagree in part with the latter. Thus the a_1 level is destabilized for *cis* bending, but for the *trans* distortion the corresponding b_u level is stabilized. In agreement with previous work[30,101] two low-lying bent configurations are available: $b_u{}^2 a_u a_g - A_u$ (becomes A_2 in C_{2v}) and $b_1{}^2 a_1 b_2 - B_2$ (becomes B_u in C_{2h}). The A_u state prefers to be *trans* bent but has a smaller potential minimum for a *cis* isomer in these calculations. The B_2 state has only one stable form—a *cis* bent molecule. The dangers of making assignments from one-electron energy gaps become apparent when it is seen that the calculations give the bent B_2 (*cis*) conformation a lower energy than the A_u (*trans*). The latter is the observed lowest singlet, the former has not yet been identified with certainty. Fixing the C—H distance at 1·10 Å, the bond variation method gives a C—C distance in the trans-bent A_u of 1·39 Å, in the cis bent B_2 of 1·37 Å. The preferred CCH angles at these distances are 145, 140° respectively. Similar calculations for diacetylene show a preference for retention of linearity in the excited state.[103a]

C_n

The models studied were linear chains, n = 1–18, and cyclic rings in the shape of regular polygons, n = 4–18, with all C≡C distances initially 1·30 Å. Total energies per carbon atom are plotted in Fig. 6. For linear chains the odd-even alternation in stability found by Pitzer[26,27] is obtained, but for large n it appears that rings will be more stable, with a new periodicity imparting particular stability to rings with $4q + 2$ members.[104] The smallest n at which a ring is preferred to a chain is 10. The change in periodicity is in qualitative agreement with the experimentally observed relative concentrations obtained from a graphite spark source[105] and the impact of focused laser beams.[106] No attempt has been made to estimate calculated abundances. The distribution of $C_n{}^-$ ions observed by Hinterberger *et al.*[105] has a different periodical behavior. Comparison of $C_n{}^-$ calculated stabilities appears to indicate that at about n = 13, $C_n{}^-$ with n = $4q + 1$ become the most stable anions, but the calculations have not been carried out for a sufficient number of large rings to confirm this trend. The gap between occupied and unoccupied levels diminishes very quickly for n = $4q$ rings, but appears to converge to a finite magnitude for n = $4q - 2$. The n odd polygons are open shell cases with an orbitally degenerate ground state configuration and should accordingly distort to less symmetrical structures.

An examination of overlap populations and charge distributions, such as those shown for C_{16} and C_{17} in Table 4, suggested that considerable bond length variation takes place. Turning to valence bond language, it seems that there are large contributions from resonance structures such as

$$:\overset{-}{C}\equiv C-\overset{+}{C}=C=C=C=C=C$$
$$:\overset{-}{C}=C-C\equiv C-\overset{+}{C}=C=C=C$$
$$:\overset{-}{C}\equiv C-C\equiv C-C=\overset{+}{C}-C=C \text{ etc.}$$

[103a] Contrary to the conclusion of G. J. Pontrelli, *J. Chem. Phys.* **43**, 2571 (1965).

[104] Polycyclic fragments of a graphite lattice, i.e. shapes similar to naphthalene, anthracene etc., are very unstable relative to simple polygons with the same number of atoms.

[105] H. Hinterberger, J. Franzen and K. D. Schuy, *Z. Naturforsch*, **18a**, 1236 (1963) and Refs therein.

[106] J. Berkowitz and W. A. Chupka, *J. Chem. Phys.* **40**, 2735 (1964).

TABLE 4. CHARGES AND OVERLAP POPULATIONS FOR C_{16} AND C_{17}, FOR (a) ALL DISTANCES EQUAL 1·30 Å, (b) THE CONVERGED DISTANCES GIVEN IN THE TEXT

| Atom	C_{16}		C_{17}	
	(a)	(b)	(a)	(b)
1	−0·8994	−0·9473	−0·9134	−0·9800
2	+0·0790	+0·0641	+0·0737	+0·0576
3	+0·2128	+0·1857	+0·2129	+0·1517
4	+0·0521	+0·0473	+0·0246	+0·0183
5	+0·1965	+0·2263	+0·2264	+0·2442
6	+0·0788	+0·0826	+0·0153	+0·0119
7	+0·1615	+0·2007	+0·2320	+0·3147
8	+0·1189	+0·1408	+0·0119	+0·0105
9			+0·2335	+0·3425
Bond				
1–2	1·6072	1·7657	1·6142	1·7873
2–3	1·2373	1·0466	1·2254	1·0210
3–4	1·4508	1·5771	1·4736	1·6306
4–5	1·3230	1·1858	1·3039	1·1343
5–6	1·3992	1·4642	1·4249	1·5309
6–7	1·3575	1·2723	1·3410	1·2268
7–8	1·3777	1·4008	1·3942	1·4306
8–9	1·3679	1·3047	1·3683	1·3269
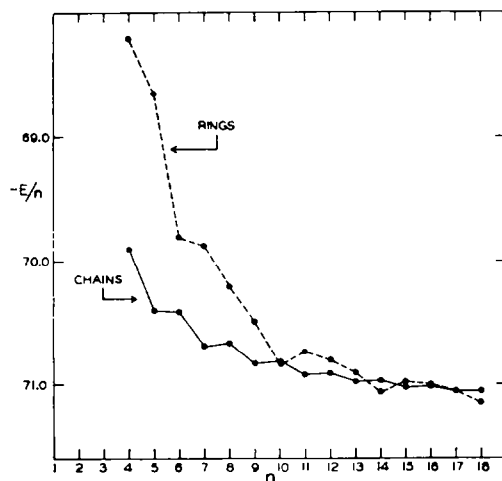
FIG. 6. Calculated stabilities of C_n linear chains and polygonal rings, all with C=C 1·30 Å.

Such structures are consistent with the direction of overlap population variation, the negative end carbons, and the persistence of *charge* alternation in the n odd species, but apparently not n even. Bond variation calculations were then done on C_2, C_3, C_4, C_{16}, C_{17}, with the following results:

C_2 : 1·229 A
C_3 : 1·295
C_4 : 1·238, 1·513
C_{16}: 1·233, 1·407, 1·267, 1·366, 1·291, 1·341, 1·306, 1·332
C_{17}: 1·229, 1·416, 1·256, 1·381, 1·276, 1·354, 1·299, 1·326

Experimental values are 1·281 for C_3,[107,108] 1·242 for C_2.[109] As concluded by Strickler and Pitzer,[27] C_4 prefers a structure better described as
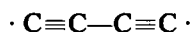
$$\cdot \, C\equiv C\!-\!C\equiv C \, \cdot$$

TABLE 5. SOME OBSERVED AND CALCULATED BOND DISTANCES IN C_3 EXCITED STATES

Observed State	Configuration zσ yσ wπ xσ vπ	Obs.	r_e (in Å) Calc. Hurley[a]	Calc. here
$1\Sigma_g{}^+$	2 2 4	1·2422	1·25	1·229
$3\Pi_u$, $1\Pi_u$	2 2 3 1	1·3117[b], 1·3180[c]	1·30	1·284
$3\Sigma_g{}^-$	2 2 2 2	1·3693	1·35	1·340
$3\Pi_g$, $1\Pi_g$	2 1 3 2	1·2660[b], 1·2730[c]	1·28	1·283
$1\Sigma_u{}^+$	2 1 4 1	1·2378	1·23	1·235
$3\Pi_g$	2 2 2 1 1	1·5350	1·54	1·510
$1\Sigma_g{}^+$	2 0 4 2	1·2518	1·21	1·239

[a] Ref. 112, [b] triplet, [c] singlet

If the C_{16}, C_{17} results reported here are reliable and if one can safely extrapolate to larger n, it appears as if bond alternation will not persist for n large, odd or even, but that the "end effect" will be great, i.e. that one will have to look quite far into the interior of the carbon chain before the bond distances settle down to a constant value. This predicted large end effect in C_n is to be contrasted with the clear bond alternation in C_nH_2 and the effective absence of alternation in C_nH_4. These results appear paradoxical, as one intuitively would expect alternation or the absence thereof for C_n, C_nH_2, C_nH_4 as n → ∞, but not the mixed behavior calculated.

In connection with the calculated preference of large polygonal rings to chains, one may note the very low bending frequency of ∼70 cm⁻¹ recently assigned to C_3.[110] The simple bending motion for C_3, with C=C 1·28 Å, was also studied here. The calculations give a slightly nonlinear C_3, with an equilibrium CCC angle of ∼160° and a very small barrier of ∼65 cm⁻¹ (0·008 ev) at the linear geometry. Since the molecule is linear[107] one should add C_3 then to the list of failures of the extended

[107] A. E. Douglas, *Astrophys. J.* **114**, 466 (1951).
[108] A. Kiess and H. P. Broida, *Canad. J. Phys.* **34**, 1471 (1956).
[109] G. Herzberg, *Molecular Spectra and Molecular Structure—I. Spectra of Diatomic Molecules* Van Nostrand, Princeton (1950).
[110] L. Gausset, G. Herzberg, A. Lagerqvist and B. Rosen, *Disc. Far. Soc.* **35**, 113 (1963).

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Hückel theory; the failure, however, is not great here—the deviation from linearity is small and in fact the molecule does bend easily.

Bond variation calculations have also been carried out on various excited states of C_2. The results are shown in Table 5 and compared with the observed distances,[111] and some calculated values from recent work by Hurley,[112] who, after Mulliken,[113] has fitted a four parameter equation which relates bond distance linearly to occupation numbers, and therefore specific bonding properties, of the individual molecular orbitals. The agreement between the calculated values and the observed is somewhat worse than that of Hurley, but it should be recalled that our calculations used a bond order-bond length curve *not fitted to any state of C_2*. The calculations cannot be fitted well by a linear formula of the Mulliken type, since the bond order-bond length curve is significantly nonlinear.

[111] After E. Clementi, *Astrophys. J.* 133, 303 (1961).
[112] A. C. Hurley in *Molecular Orbitals in Chemistry, Physics and Biology* (Edited by P. O. Löwdin and B. Pullman) p. 161. Academic Press, New York (1964).
[113] R. S. Mulliken, *Phys. Rev.* 56, 778 (1939).