Calculation of the Structures of Hydrocarbons Containing Delocalized Electronic Systems by the Molecular Mechanics Method[1,2]

Norman L. Allinger[3] **and Joseph T. Sprague**[4]

Departments of Chemistry, University of Georgia, Athens, Georgia 30601,
and Wayne State University, Detroit, Michigan 48202.

Received September 5, 1972

Abstract: The molecular mechanics method for structure determination has been extended to hydrocarbons containing delocalized systems by including a quantum mechanical (VESCF) π-system calculation in the iterative sequence, from which bond orders are obtained. A relationship between stretching force constant and bond order is found, so the force constants can be calculated from the bond orders, and the delocalized molecule is then handled in the standard way. Torsional constants are calculated from the planar molecule, and then the molecule is allowed to deform to the geometry corresponding to an energy minimum. Thus the method is applicable to nonplanar systems as well as to planar systems. It is applied to many simple compounds (butadiene, benzene, biphenyl, naphthalene, etc.), and then to more complicated systems such as *o*-di-*tert*-butylbenzene, pregeijerene, the annulenes, and bridged annulenes. Insofar as experimental data are available, the agreement with experiment is generally good. In a few cases structural predictions are made.

Previous papers have described a force field method for the calculation of the structures and energies of saturated hydrocarbons,[5] ketones,[6] and olefins.[7] There seems no doubt that the method is generally applicable to the calculation of the structures of molecules, but there are areas where special problems occur, ones which require something substantially more than the kind of treatment used in the cases discussed. Aromatic compounds, and other compounds containing delocalized systems, are found to present such problems. Hydrocarbons will be dealt with in this paper, and the extension to other kinds of compounds such as unsaturated ketones, etc., will be the subject of subsequent papers.

The basic problem can perhaps best be seen by considering some simple examples. If one wishes to treat a delocalized system such as benzene by the force field method, as long as one knows the force constants, the method is straightforward. For benzene, since all of the bonds are equivalent, the force constants can be evaluated by standard methods. They can then be applied to those benzene derivatives where the substituents on the benzene are not sufficient to interrupt the conjugated electronic system so as to change any stretching constants or natural bond lengths or angles. However, if one considers the naphthalene molecule as another example, one finds the following. If the benzene stretching constants and bond lengths are used, it is found that one calculates all of the bond lengths in naphthalene to be approximately equal in length, similar to those in benzene. This is not correct, as it is well known that some of the bonds are a good deal longer than others. The bond lengths are closely related to the π-bond orders.[8]

In considering how one might obtain the necessary force constants in a general way for delocalized systems, it seemed that one approach would be to take the preliminary geometry and do a π-system calculation to find the bond orders, which should be related to the force constants. If the relationships were known, the force constants would be available, and then a system such as naphthalene could be treated by the standard molecular mechanics method. If in the process of minimizing the energy the geometry changed very much from the initially assumed geometry, then the π-bond orders would also change, along with the force constants. An iterative scheme would then be necessary so as to bring to internal consistency the geometry, bond orders, and force constants when the energy minimum was reached. The validity of this method would hinge upon the bond order–force constant relationships, the most important one being that involving the bond lengths. While the latter is known to be reasonably good, there appears to be in the literature some cases where it gives results which are outside of experimental error. It was therefore felt necessary at the outset to establish that such a relationship was sufficiently accurate for our purposes, and also to decide exactly which variant of the available relationships should be used. The selection of bond order relationships involving other force constants (such as bending and torsion) is an entirely different matter, since there is little useful literature data concerning them.

The method proposed above has both strengths and weaknesses. π-System calculations have been carried out in great detail over the years. The approximations involved have been exhaustively examined theoretically,

---

(1) This is paper XC in the series "Conformational Analysis" [paper LXXXIX: N. L. Allinger and N. A. Pamphilis, *J. Org. Chem.*, **38**, 316 (1973)] and paper XXX in the series "Organic Quantum Chemistry" [paper XXX: N. L. Allinger and J. C. Graham, *J. Amer. Chem. Soc.* **95**, 2523 (1973)], presented at the International Conference on Conformational Analysis, Paris, France, June 1970, and at the 161st Natiional Meeting of the American Chemical Society, Los Angeles, Calif., March 1971, Abstract ORGN 5.

(2) This research was supported in part by Grant No. GP-15263 from the National Science Foundation.

(3) Correspondence should be addressed to this author at the University of Georgia.

(4) National Science Foundation Predoctoral Fellow, 1969–1970.

(5) N. L. Allinger, M. T. Tribble, M. A. Miller, and D. H. Wertz, *J. Amer. Chem. Soc.*, **93**, 1637 (1971).

(6) N. L. Allinger, M. T. Tribble, and M. A. Miller, *Tetrahedron*, **28**, 1173 (1972).

(7) N. L. Allinger and J. T. Sprague, *J. Amer. Chem. Soc.*, **94**, 5734 (1972).

(8) This subject has been dealt with fairly extensively over the years. The information is summarized by Allinger and Graham (ref 1).

and the calculations have been applied to almost every conceivable situation. In the present case, the crucial question is the accuracy of the bond order–bond length relationship within the framework of the detailed method chosen. As a prelude to this study, Graham[8] carried out a detailed examination of the bond order–bond length relationship within the framework of the Hückel method, the standard SCF method, and the VESCF method. It was found that the VESCF method gave a bond order–bond length relationship which enabled the calculation of geometries for a variety of relatively strainless molecules with as good or better accuracy than any other method. Since this method has the additional advantage that it can be used subsequently to calculate the electronic spectrum of the conjugated system, it was chosen for use in the present work. The VESCF method, originally introduced by Brown,[9] was developed for hydrocarbons in earlier papers.[10] The method is clearly extendable in principle to molecules containing other atoms, and to electronically excited states. Core ionization potentials appropriate for other atoms can be found from spectroscopic data or by CNDO-type calculations.

This method has the advantage of being very fast in terms of computer time compared to any kind of an all-electron quantum mechanical calculation which is iteratively used to minimize the energy of the molecule, since the SCF calculation is carried out only on the π system, not on the whole molecule, and the actual minimization iterates over simple empirical functions, and not over the SCF sequence. Thus the time required for minimizing the energy of the molecule by this method is less by two or three orders of magnitude than it would be by an all-electron scheme. In terms of the accuracy of the results, the MINDO method of Dewar is the only all-electron calculation that has been studied in very much detail.[11] That method utilizes complete neglect of differential overlap in the integrals calculation, and an empirical evaluation of integrals in an attempt to both simplify the *ab initio* type approach and to obtain results that are in accord with experience, rather than in accord with the Hartree-Fock limit of calculational accuracy. From the published data, we believe our structures and energies are about one order of magnitude more accurate than those obtained by the MINDO method, and the time required for the calculation is two or three orders of magnitude less. These are the strengths of this method.

The weaknesses are that one must somehow have available the necessary force constants for the rest of the system which is not being dealt with in the π calculation. This would include interactions of the π system with the rest of the molecule as well as those interactions within the π system whose force constants are not functions of the π calculations. Also, as in other molecular mechanics calculations, the limits to which the force field is valid cannot be exceeded.

The Method. In general, to determine the structure of a molecule containing a delocalized system by calculation, it is necessary to do some kind of quantum mechanical treatment of the π system. If the σ–π separation is an acceptable approximation, as it ordinarily is for planar systems, then the calculational procedure which should contain the minimum amount of numerical work, and yet lead to an acceptable force field, would be to treat the σ system by means of the usual molecular mechanics methods, and use the π-system calculations to modify certain of the force constants coming into the calculation. Even though it seems clear enough in principle what one might do, there are in practice a number of problems.

Nonbonded interactions involving C_{sp^2} atoms, for example, are expected to be somewhat dependent on the charge density of the p_π orbital. Owing to the empirical nature of the van der Waals function and the lack of any pertinent experimental data for C_{sp^2} atoms, however, there is no reasonable way of assigning this dependency. Consequently, C_{sp^2} parameters based on graphite have been used for all unsaturated centers. In view of the fact that hydrocarbon π-charge densities are very close to unity, this seems to be a reasonable approximation.

Bending parameters should also be a function of the charge distribution (even assuming the absence of small hybridization changes) since the bending function is used to account for 1,3-nonbonded interactions. As was the case with small olefins,[7] however, there are very little data available regarding force constants; consequently, we have used the bending constants[5] appropriate for saturated and unsaturated hydrocarbons here also. Any parameters not specifically mentioned were taken from earlier papers.[5,7] In addition, structural data for conjugated π systems are too insensitive to establish any natural angle (θ_0) relationships; therefore, the 120° value has been assumed for the natural angle (θ_0) about all C_{sp^2} atoms bonded to two unsaturated centers.

The dependence of bond lengths on the π-electron distribution has been recognized for some time, as evidenced by the existing variety of bond order relationships. Such relationships seem intuitively correct, since bond orders are a measure of the electron density between π centers, and in terms of binding forces in molecules, we would expect this force to change as the π-electron density between the atoms changes. The problem, of course, is determining the exact form of this relationship.

In molecular orbital theory, bond orders (p_{ij}) are defined as

$$p_{ij} = \sum N c_i c_j \qquad (1)$$

where N is the number of electrons in each of the occupied orbitals and c_n is the coefficient for the atomic orbital. A variety of empirical relationships have been proposed. They have been reviewed by Trotter[12] and generally they are of the form

$$l = l_1 - r p_{ij} \qquad (2)$$

where l_1 and r must be empirically determined. Most of these relationships, using Hückel and SCF bond orders, give good results for a number of planar alternate hydrocarbons.

In the present work, we set out to determine a relationship of the form of eq 2 which would supply natural bond lengths (l_0) to the force field, which in turn would

---

[9] R. D. Brown and M. L. Heffernan, *Aust. J. Chem.*, 12, 319 (1959).

[10] N. L. Allinger and J. C. Tai, *J. Amer. Chem. Soc.*, 87, 2081 (1965); N. L. Allinger, J. C. Tai, and T. W. Stuart, *Theor. Chim. Acta*, 8, 101 (1967).

[11] M. J. S. Dewar and E. Haselbach, *J. Amer. Chem. Soc.*, 92, 590 (1970), and other papers in this series.

be at least capable of duplicating the results of other bond order–bond length relationships.[8,12] The experimental geometries of ethylene, butadiene, and benzene (see Table I) were chosen to establish the relationship 2, since they are simple structures for which accurate data are available. The natural bond lengths required by the force field to duplicate these experimental results were plotted against the VESCF bond orders to obtain the relationship

$$l_0 = 1.511 - 0.179\,p_{ij} \tag{3}$$

The required values of l_0, their corresponding p_{ij}, and the values of l_0 corresponding to eq 3 are listed in Table II.

Table I. Ethylene, Butadiene, and Benzene Geometries

	C=C length, Å	C—C length, Å	Method	Ref
Ethylene	1.337 ± 0.001		ED	*a*
	1.339 ± 0.002		Raman	*b*
	1.337 ± 0.003		Ir	*c*
	1.337		Optimum	
Butadiene	1.341 ± 0.002	1.463 ± 0.003	E.D.	*d*
	1.344 ± 0.001	1.467 ± 0.001	E.D.	*e*
	1.343	1.466	Optimum	
Benzene	1.392 ± 0.003		X-Ray	*f*
	1.397		X-Ray	*g*
	1.397 ± 0.001		Raman	*h*
	1.397		Optimum	

[a] L. S. Bartell, E. A. Roth, C. D. Hollowell, K. Kuchitsu, and J. E. Young, Jr., *J. Chem. Phys.*, **42**, 2683 (1965). [b] J. M. Dowling and B. P. Stoicheff, *Can. J. Phys.*, **37**, 703 (1959). [c] H. C. Allen and E. K. Plyler, *J. Amer. Chem. Soc.*, **80**, 2673 (1958). [d] K. Kuchitsu, T. Fukuyama, and Y. Morino, *J. Mol. Struct.*, **1**, 463 (1968). [e] W. Haugen and M. Traetteberg, *Acta Chem. Scand.*, **20**, 1726 (1966). [f] E. G. Cox, D. W. J. Cruickshank, and J. A. S. Smith, *Proc. Roy. Soc., Ser. A*, **247**, 39 (1958). [g] A. Almenningen, O. Bastiansen, and L. Fernholt, *Kgl. Nor. Vidensk. Selsk. Skr.*, No. 3 (1958). [h] A. Langseth and B. P. Stoicheff, *Can. J. Phys.*, **34**, 350 (1956).

Table II

Compd	Exptl length, Å	Required l_0	VESCF p_{ij}	Calcd l_0
Ethylene	1.337	1.330	1.0	1.332
Butadiene	1.343	1.336	0.951	1.341
Butadiene	1.466	1.456	0.309	1.456
Benzene	1.397	1.393	0.667	1.392

This relationship defines the natural length of a zero bond order C_{sp^2}–C_{sp^2} bond as 1.511 Å. It might be noted that a C_{sp^2}–C_{sp^2} single bond length of 1.52 ± 0.01 Å (ω = 90 ± 10°) is found in hexaphenylbenzene.[13] While steric effects are certainly present in this molecule, it is doubtful that they result in any significant stretching of this bond.

The stretching force constant (k_s) should also be related to the bond order, in that it is a measure of the binding energy between the atoms. Although *a priori* there is no reason to suspect that the relationship is linear, experimental evidence indicates that it is at least fairly close to being so.[14–16] Unfortunately, for C_{sp^2}–C_{sp^2} bonds the only useful experimental data available are the ethylene k_s of 9.6 × 10^{-5} dyn/cm[17] and a benzene k_s of 7.6 × 10^{-5} dyn/cm.[18] Assuming a linear relationship, a plot of p_{ij} *vs.* k_s results in a force constant of 3.6 × 10^{-5} dyn/cm for a C_{sp^2}–C_{sp^2} single bond ($p_{ij} = 0$) which is considerably below Herzberg's C_{sp^3}–C_{sp^3} constant of 4.5 × 10^{-5} dyn/cm.[17] This seems intuitively incorrect since the σ overlap of sp^2 and sp^3 orbitals is almost identical at distances of 1.5–2.0 Å.[19] It is acknowledged,[14,17] however, that transferable force constants for polyatomic groups are certainly not accurate to better than about 10% due to approximations in the force fields used to calculate them. Thus, assuming a benzene force constant of 8.1 × 10^{-5} dyn/cm, the relationship becomes

$$k_s = 5.0 + 4.6p_{ij} \tag{4}$$

where the C_{sp^2}–C_{sp^2} single bond force constant is 5.0 × 10^{-5} dyn/cm. Although this relationship was finally settled on for rather arbitrary reasons, it is doubtful that it could result in any detectable errors in calculated results, since geometries are insensitive to small changes in k_s.

As was mentioned earlier,[7] the torsional function across a double bond is used to measure the π-bond disruption as rotation occurs about the bond. For simple rotations of C_{sp^2}–C_{sp^2} single bonds, such as in butadiene and biphenyl, the *conjugation energy* may be defined as

$$E_{\text{conj}}(\omega) = E(\omega) - E(90°) \tag{5}$$

where $E(\omega)$ is the π-electronic energy of the conformation with a dihedral angle, ω. It is found that values for E_{conj} are well reproduced by the simple formula[20]

$$E_{\text{conj}}(\omega) \approx E_{\text{conj}}(0°)\cos^2\omega \tag{6}$$

If there is a way of determining the E_{conj} (0°), then we may describe the π-electronic hindrance to rotation with a simple ($\cos^2$) torsional function similar to that used for ethylene.[7] As it is impractical as well as inaccurate to calculate this quantity for any bonds other than central bonds in simple systems, such as butadiene and biphenyl, we must find some alternative method of estimating E_{conj} for the various C_{sp^2}–C_{sp^2} bonds in a π system. The most obvious solution would of course be a relationship based on bond orders.

If we consider a closed system, the total energy of the π system in the HMO approximation may be expressed as[21]

$$E_\pi = \sum_i q_i\alpha_i + 2\sum_{i<j}\sum p_{ij}\beta_{ij} \tag{7}$$

where α_i is the binding energy of an electron in the AO ϕ_i and there are q_i electrons in this region. We may think of β_{ij} as the π energy of an electron in the overlap

---

(12) J. Trotter, *Roy. Inst. Chem. Lect. Ser.*, No. 2, 1 (1964).

(13) A. Almenningen, O. Bastiansen, and P. N. Skancke, *Acta Chem. Scand.*, 12, 1215 (1958).

(14) E. A. Robinson and M. W. Lister, *Can. J. Chem.*, 41, 2988 (1963).

(15) R. J. Gillespie and E. A. Robinson, *Can. J. Chem.*, **41**, 2074 (1963).

(16) E. M. Popov and G. A. Kogan, *Theor. Exp. Chem. (USSR)*, 1, 295 (1965).

(17) G. Herzberg, "Molecular Spectra and Molecular Structure," Van Nostrand, Princeton, N. J., 1945, p 193.

(18) R. C. Lord and D. H. Andrews, *J. Phys. Chem.*, 41, 149 (1937).

(19) J. D. Roberts, "Molecular Orbital Calculations," W. A. Benjamin, New York, N. Y., 1961, p 30.

(20) I. Fischer-Hjalmars, *Tetrahedron*, 19, 1805 (1963).

(21) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969, p 194.

region between AO's ϕ_i and ϕ_j and there are $2p_{ij}$ electrons in this region. The contribution to the π energy of the overlap charge between atoms i and j is thus $2p_{ij}\beta_{ij}$. As the bond C_i–C_j in a conjugated system is twisted, both p_{ij} and β_{ij} will approach zero. We may therefore estimate that the E_{conj} between atoms i and j is approximately proportional to p_{ij}^2. The only experimental quantities available to test this approximation are the rotational barriers for ethylene,[22] stilbene,[23] and butadiene.[24] The function

$$E_{\text{conj}} = 54.2p_{ij}^2 \text{ kcal/mol} \qquad (8)$$

was chosen to represent these data. (These three points could in fact be better fit by a larger constant (about 59), but the value chosen was later found to give better results over a range of nonplanar structures.)

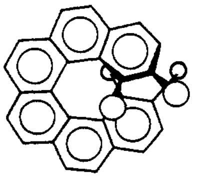
From eq 8 we can calculate that portion of the barrier to rotation of a simple conjugated system which is due to the disruption of conjugation across the rotated bond. Using this barrier in a torsional function derived from eq 6 allows our mechanical model to describe distortions in a π system.

The strain energy, E_s, is defined[7] in terms of energy differences from those obtained with "normal" sets of parameters. For a conjugated molecule this means that the torsional energy representing the π system disruption is defined in terms of a planar structure, since the "normal" torsional parameters for X–C_{sp^2}–C_{sp^2}–X bonds favor 0 and 180° dihedral angles. If we begin calculations on a nonplanar π system, then the torsional energy calculated for the π-bond disruptions will be based on an erroneous E_{conj} since eq 8 is derived from data representing

$$E_{\text{conj}} = E(0°) - E(90°) \qquad (9)$$

This means the torsional constants must be derived from bond orders calculated for a planar π system. Since many of the molecules which we wished to study require initial nonplanar π systems for the molecular mechanics calculation, we were forced to develop some method of approximating their corresponding planar conformations.

The only function of atomic coordinates in a Pariser–Parr–Pople (PPP) calculation is to establish distances and direction cosines between orbital pairs. The problem is: how may we adjust the distances and direction cosines in a PPP calculation in order to reasonably approximate the planar form of a nonplanar system? Hexahelicene serves as an excellent example of what errors may occur in various approximations.



hexahelicene

In this molecule, the "planar" form should display the following features: all p_π orbitals should be parallel to one another and perpendicular to a common plane; there should be no appreciable π overlap between the terminal rings; all bound atom distances should correspond to those of the nonplanar structure. The p_π orbital orientation may be accomplished by making all $\cos \beta_1 = \cos \beta_2 = 1$ and all other direction cosines equal to zero. This, however, will result in anomalous (terminal ring) overlap. The most generally valid compromise is to change only bound atom direction cosines and retain all of the nonplanar bound and nonbound distances.

The Minimization Scheme

The energy minimization sequence for a conjugated molecule is considerably more complicated than for a simple olefin. The procedure is basically as follows. From input data the molecular geometry is calculated and all parameters not dependent on bond orders are assigned. A VESCF calculation is then undertaken and the resulting bond orders are used to assign stretching parameters according to the previously described relationships. If the molecule is nonplanar, the previously described modifications are made to the direction cosines and a second VESCF calculation is undertaken in order to obtain bond orders suitable for establishing torsional constants. The steric energy is then minimized with respect to geometry according to the procedure outlined earlier.[5] If the geometry has been significantly changed during the minimization, one might reasonably expect some change in the π system. The VESCF calculations are therefore repeated and the new bond orders are used to assign new stretching and torsional parameters. The minimization–VESCF cycle is repeated until total self-consistency is reached. After the initial cycle, the changes become quite small and the minimization proceeds quite rapidly.

Computer times vary according to the size of the molecule with a 30 atom, 14π-orbital system requiring a few minutes of cpu time on the IBM 360/65.

Results

We began our studies with butadiene since it is one of the few conjugated molecules for which a variety of structural and thermodynamic data are available. As seen in Table III, our calculated geometry agrees quite well with the most recent experimental data.

Table III. Butadiene Geometries

C═C, Å	C—C, Å	∠C═C—C, deg	Ref	Method
1.337 ± 0.005	1.483 ± 0.010		*a*	ED
	1.476 ± 0.01	122.9 ± 0.5	*b*	Raman, Ir
(1.338)	1.464 ± 0.003	(123.2)	*c*	Ir
1.3439 ± 0.0005	1.4672 ± 0.0013	122.86 ± 0.5	*d*	ED
1.341 ± 0.002	1.463 ± 0.003	123.3 ± 0.5	*e*	ED
1.346	1.468	122.3		Calcd

[a] A. Almenningen, O. Bastiansen, and M. Traetteberg, *Acta Chem. Scand.*, **12**, 1221 (1958). [b] D. J. Marais, N. Sheppard, and B. P. Stoicheff, *Tetrahedron*, **17**, 163 (1962). [c] A. R. H. Cole, G. M. Mohay, and G. A. Osborne, *Spectrochim. Acta, Part A*, **23**, 909 (1967). [d] Footnote *e*, Table I. [e] Footnote *d*, Table I.

While the butadiene geometry is interesting in that it serves to generally verify our initial parameter assignments and relationships, of greater interest is its rota-

---

(22) J. E. Douglas, B. S. Rabinovitch, and F. S. Looney, *J. Chem. Phys.*, 23, 315 (1955).

(23) G. B. Kistiakowsky and W. R. Smith, *J. Amer. Chem. Soc.*, **56**, 638 (1934).

(24) J. G. Aston, G. Szasz, H. W. Woolley, and F. G. Brickwedde, *J. Chem. Phys.*, **14**, 67 (1946).

tional potential about the C_{sp^2}–C_{sp^2} single bond. A number of years ago the total potential was evaluated[24] from selected spectroscopic and thermodynamic data. The barrier to rotation was calculated to be 4.9 kcal/mol with the s-trans form favored over the s-cis by 2.3 kcal/mol, and similar values are given by *ab initio* calculations.[25] Chemical[26] and nmr[27] data support the cis/trans ratio.

The empirical potential function which spectroscopists generally use to describe the hindrance to internal rotation around a C–C bond is the series

$$V(\omega) = \frac{V_1}{2}(1 - \cos \omega) + \frac{V_2}{2}(1 - \cos 2\,\omega) + \frac{V_3}{2}(1 - \cos 3\,\omega) \quad (10)$$

where terms higher than the third are assumed to be insignificant. For the C_{sp^2}–C_{sp^2} single bond, V_1, V_2, and V_3 may all have nonzero values, and because we have placed no limitations on the range of ω, all of these terms may be required in this torsional function. The relative energies of the s-cis, 90°, and s-trans forms of butadiene, however, are insufficient to define these terms since the shape of the potential between energy minima and maxima is uncertain and the dihedral angles of the first two forms are only assumed to be exactly 0 and 90°.

What is measured spectroscopically is the torsional constant, V^*. For butadiene it has the value 28.1 kcal/mol.[28] This constant, however, refers only to the shape of the minimum at 180° and is a function of the three constants V_1, V_2, and V_3. In this relationship[28]

$$V^* = \pm|V_1| \pm 4|V_2| \pm 9|V_3| \quad (11)$$

the sign before the coefficient is (+) if the term is at an energy minimum for the ground-state conformation, and is (−) for an energy maximum. Now, our mechanical model describes hindrance to internal rotation in terms of nonbonded interactions plus a torsional function. The nonbonded interactions in butadiene are found to yield a function in the form of eq 10 with $V_1 = -1.30$, $V_2 = -1.47$, and $V_3 = 0$. Obtaining a conjugation energy from eq 8 and rewriting eq 6 in a more convenient form, our torsional function may also be expressed in the form of eq 10 with $V_1 = V_3 = 0$, and $V_2 = 4.95$ kcal/mol. Several discrepancies resulted from this latter function, however. First of all, our calculated V^* is only 15.22 kcal/mol,[29] and second, our calculated s-trans − s-cis energy difference is only 1.30 kcal/mol with a 3.48 kcal/mol barrier to interconversion. We could resolve these differences with $V_3 = -1$ kcal/mol, as this would allow us to duplicate the experimental s-trans − s-cis energy difference as well as increase the calculated V^* to 24.2 kcal/mol. We are at quite a loss, however, to explain the origin of a threefold term across a C_{sp^2}–C_{sp^2} bond. It is instead felt more reasonable to assume that a V_1 term is responsible for the extra s-trans − s-cis energy difference, and that a small V_4 term is responsible for the large experimental V^*. We have chosen to include a 1 kcal/mol V_1 term since it is the only reasonable way to account for the 2.3 kcal/mol s-trans − s-cis difference, but have avoided trying to duplicate the experimental V^* with additional terms, since the pertinent experimental data are insufficient. It is important to note that small positive V_2 and V_4 terms will have little effect on our calculated geometries and steric energies.

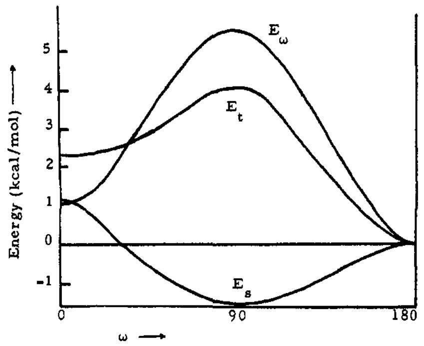


Figure 1. The barrier to rotation in butadiene: E_ω is the torsional energy, E_s the steric energy, and E_t is the sum.

The components of our calculated butadiene rotational barrier are shown in Figure 1. The conjugation across the central bond is found to be the principal cause of the planarity of this molecule and is responsible for the 3.98-kcal/mol rotational barrier. The s-trans − s-cis energy difference of 2.30 kcal/mol results from approximately equal amounts of torsional and nonbonded interactions.

The C_{sp^2}–C_{sp^2} torsional function actually used in our calculations, then, is

$$V(\omega) = \frac{V_1}{2}(1 + \cos \omega) + \frac{V_2}{2}(1 - \cos 2\omega) \quad (12)$$

where V_1 is 1 kcal/mol, and V_2 is one-fourth the E_{conj} of eq 8 for the central bond of the angle. This factor of 4 is used since the total barrier is treated as four individual barriers of substituent pairs and each of these is allowed to account for one-fourth of the bond E_{conj}. The sign in the first term has been changed from eq 10 making the C_{sp^2}/C_{sp^2} torsional interaction positive in order to be consistent with the C_{sp^3}–C_{sp^3} functions, and every dihedral angle with a C_{sp^2}–C_{sp^2} bond is an operand of eq 12 in the way that every aliphatic dihedral angle is an operand of the previously discussed third-order function.[5,7]

Next, in order to verify our bond order–bond length relationship, the structures of a series of planar, aromatic hydrocarbons were calculated and the results were compared with structures obtained by other methods. For naphthalene[30] and anthracene[31] the calculated bond lengths were within the standard deviations in the X-ray data. The other results are summarized in Table IV. Geometries are for the most part correct to within experimental error, but there is no net improvement over results obtained by other simple bond order–bond length methods. This, of

---

[25] L. Radom and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 4786 (1970).

[26] W. B. Smith and J. L. Massingill, *J. Amer. Chem. Soc.*, **83**, 4301 (1961).

[27] A. A. Bothner-By and R. K. Harris, *J. Amer. Chem. Soc.*, **87**, 3451 (1965).

[28] W. G. Fateley, R. K. Harris, F. A. Miller, and R. E. Witkowski, *Spectrochim. Acta*, **21**, 231 (1965).

[29] $V^* = V_1^{nb} + 4(V_2^{nb} + V_2^{tors}) + 9V_3^{nb}$

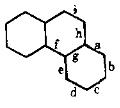
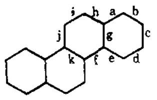
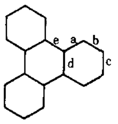
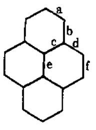
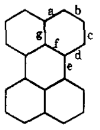
$= 1.30 + 4(4.95 - 1.47) + 0$

$= 15.22$

[30] A. Almenningen, O. Bastiansen, and F. Dyvik, *Acta Crystallogr.* **14**, 1056 (1961).

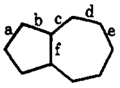
[31] R. Mason, *Acta Crystallogr.*, **17**, 547 (1964).

Table IV. Aromatic Hydrocarbon Geometries[a]

	Bond	Exptl	SCF	Calcd	Calcd − Exptl
		b, c	*d, f*		
Phenanthrene	a	1.457 ± 0.014	1.419	1.417	−0.040
	b	1.381 ± 0.014	1.387	1.382	0.001
	c	1.398 ± 0.014	1.414	1.406	0.008
	d	1.383 ± 0.014	1.388	1.386	0.003
	e	1.405 ± 0.014	1.418	1.418	0.013
	f	1.448 ± 0.020	1.448	1.457	0.009
	g	1.404 ± 0.014	1.412	1.412	0.008
	h	1.390 ± 0.014	1.443	1.440	0.050
	i	1.372 ± 0.020	1.365	1.362	−0.010
		g	*c, d*		
Chrysene	a	1.427	1.422	1.420	−0.007
	b	1.367	1.385	1.379	0.018
	c	1.392	1.416	1.409	0.017
	d	1.379	1.385	1.383	0.004
	e	1.408	1.421	1.424	0.019
	f	1.465	1.442	1.452	−0.013
	g	1.406	1.414	1.411	0.005
	h	1.418	1.438	1.431	0.013
	i	1.365	1.371	1.366	0.001
	j	1.423	1.435	1.437	0.014
	k	1.397	1.402	1.406	0.009
		h	*c, d*		
Triphenylene	a	1.416 ± 0.004	1.412	1.416	0.0
	b	1.377 ± 0.005	1.393	1.387	0.010
	c	1.402 ± 0.007	1.408	1.397	−0.005
	d	1.415 ± 0.006	1.410	1.412	−0.003
	e	1.447 ± 0.006	1.456	1.468	0.021
		i	*c, d*		
Pyrene	a	1.380 ± 0.011	1.399	1.395	0.015
	b	1.420 ± 0.009	1.409	1.406	−0.014
	c	1.417 ± 0.007	1.421	1.416	−0.001
	d	1.442 ± 0.009	1.446	1.445	0.003
	e	1.417 ± 0.014	1.434	1.431	0.014
	f	1.320 ± 0.014	1.363	1.363	0.043
		j	*c, d*		
Perylene	a	1.400 ± 0.004	1.427	1.423	0.023
	b	1.370 ± 0.005	1.383	1.375	0.005
	c	1.418 ± 0.004	1.417	1.411	−0.007
	d	1.397 ± 0.004	1.391	1.393	−0.004
	e	1.471 ± 0.004	1.461	1.473	0.002
	f	1.425 ± 0.003	1.429	1.431	0.006
	g	1.424 ± 0.004	1.418	1.417	−0.007

[a] In general, the molecules in Table IV were assumed to be planar, and so constrained in the calculations. For perylene, when the molecule was constrained to have instead a C_2 axis which included bond g, it was found that when the top half of the molecule was twisted in one direction about this axis, and the bottom half twisted in the other direction, and the energy was minimized, the carbons at the c, d and symmetry related junctions were found out of the average molecular plane by ±0.197 Å, and their attached hydrogens by ±0.291 Å. The twisted form had 1.2 kcal/mol less van der Waals repulsion than did the planar form, but 1.2 kcal/mole more torsional energy. Thus the calculations indicate a torsional motion of this kind of wide amplitude can occur with essentially no change in energy. When phenanthrene was similarly deformed by moving carbons 1 and 8 in opposite directions perpendicular to the molecular plane, and holding them out of the plane, but minimizing the energy of the remainder of the structure, it was found that the planar form corresponded to the energy minimum, but that a dihedral angle between carbons 1 and 8 of 5° raised the energy by only 0.05 kcal/mol, while a dihedral angle of 10.7° raised the energy 0.24 kcal/mol. The torsional barrier is higher here than in perylene, because the bond is shorter, so there is an increased tendency for the molecule to be planar. It seems likely that for all the structures in Figure 2, and other similar molecules as well, the energy differences between the planar and nonplanar forms are very small. The exact degree of planarity in such molecules in crystals is therefore expected to be determined by lattice forces. [b] J. Trotter, *Acta Crystallogr.*, **16**, 605 (1963). [c] Subsequent to the completion of this work, because of the disagreement between the calculated and experimental values for the bond lengths in phenanthrene after all steric interaction, etc., had been allowed for, we concluded that the molecule could not have in the gas phase the bond lengths specified for it by Trotter. (This was also suggested by Lo and Whitehead[d] on the basis of calculations which did not properly allow for steric interactions.) Such bond lengths could not be ruled out for the molecule in the crystal by theoretical considerations, but we felt they were most improbable, and therefore undertook an X-ray study of the phenanthrene crystal in February 1971, in collaboration with Professor M. G. Newton and Miss M. Raut. Before this work was completed, another very thorough study of phenanthrene was published[e] based on X-ray and neutron diffraction data. This new structure agrees to within experimental error with the experimental bond lengths listed in this table except for bond a which is now reported as 1.428 (9) (X-ray) and 1.417 (21) (neutron), and bond h which is 1.450 (7) (X-ray) and 1.455 (39) (neutron). The numbers in parentheses are the differences between the two bonds which were averaged to get a symmetrical structure. The standard deviations for their experimental bond lengths are about 0.009 Å. It can be seen that these new values are in good agreement with our calculated structure. We believe that the experimental values for the bond length f in pyrene and probably bond a in perylene are similarly wrong. Note that the bond length for bond e in perylene, which is very long for an aromatic bond, is accurately calculated here. [d] D. H. Lo and M. A. Whitehead, *Can. J. Chem.*, **46**, 2027, 2041 (1968). [e] M. I. Kay, Y. Okaya, and D. E. Cox, *Acta Crystallogr., Sect. B*, **27**, 26 (1971). [f] An SCF approach employing a σ- and π-energy minimization after each iteration until an absolute minimum is reached. New bond lengths are calculated from an energy–bond length relationship. [g] D. M. Burns and J. Iball, *Proc. Roy. Soc., Ser. A*, **257**, 491 (1960). [h] F. R. Ahmed and J. Trotter, *Acta Crystallogr.*, **16**, 503 (1963). [i] A. Camerman and J. Trotter, *Acta Crystallogr.*, **18**, 636 (1965). [j] A. Camerman and J. Trotter, *Proc. Roy. Soc., Ser. A*, **279**, 129 (1964).

Table V. Azulene Geometry



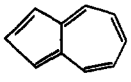
Bond	X-Ray[a,b] Robertson	X-Ray[c,d] Hanson	Electron[e] diffraction	VESCF[8]	Calcd
		Bond, Å			
a	1.425 ± 0.032 1.363 ± 0.027	1.394 ± 0.004	1.399 ± 0.009	1.400	1.394
b	1.459 ± 0.024 1.378 ± 0.019	1.398 ± 0.004	1.418 ± 0.010	1.405	1.403
c	1.369 ± 0.007 1.395 ± 0.005	1.391 ± 0.004	1.383 ± 0.008	1.408	1.405
d	1.440 ± 0.021 1.337 ± 0.034	1.400 ± 0.004	1.406 ± 0.016	1.400	1.401
e	1.422 ± 0.026 1.337 ± 0.035	1.392 ± 0.005	1.403 ± 0.014	1.402	1.404
f	1.483 ± 0.004	1.498 ± 0.004	1.501 ± 0.005	1.479	1.463
		Angle, deg			
b–f	106.3	106.2 ± 0.5			106.8
c–f	127.4	128.6 ± 0.6			128.3
c–d	129.3	127.3 ± 1.3			127.8

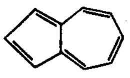
[a] C_{2v} symmetry has been the result of most measurements and calculations. If two entries appear as data, the molecule has been found to be unsymmetrical in that experiment. [b] J. M. Robertson, H. M. M. Shearer, G. A. Sim, and D. G. Watson, *Acta Crystallogr.*, **15**, 1 (1962). [c] These are mean values. [d] A. W. Hanson, *Acta Crystallogr.*, **19**, 19 (1965). [e] O. Bastiansen and J. L. Derissen, *Acta Chem. Scand.*, **20**, 1319 (1966).

course, implies that the bond lengths in these compounds are determined primarily by conjugation rather than steric effects, and indicate that this is the best that can be done within the limits of bond order–bond length methods and/or experimental error.

The only notable steric interaction found in these molecules is the phenanthrene-type H···H overcrowding (Figure 2). Through small changes spread throughout the molecule, however, these interactions are much less severe than one might first suspect from models. In phenanthrene, chrysene, triphenylene, and perylene, each interaction amounts to 1.25–1.75 kcal/mol which confirms a 1.5 kcal/mol estimate derived from hydrogen–deuterium exchange constants and the basicities of the hydrocarbons' conjugate bases.[32] The C_{sp^2}–C_{sp^2} bond in each of these cases is stretched about 0.015 Å from the natural length. Coulson suggested[33,34] that the overcrowding of the hydrogen atoms cannot be responsible for the experimentally observed increases in the peri bonds in perylene, assuming the van der Waals radius of hydrogen was only 1.2 Å. When a more realistic van der Waals radius is used, it is found that the stretching from this cause is quite significant, but the low bond order is a major factor also.

Azulene is also an interesting test molecule for which there are some experimental data available, although crystal disorder leads to some problems. Since azulene satisfies the Hückel ($4n + 2$) condition and has no Kekulé form with an internal double bond, its Kekulé forms lead one to suspect that the peripheral bonds are fairly regular in length.





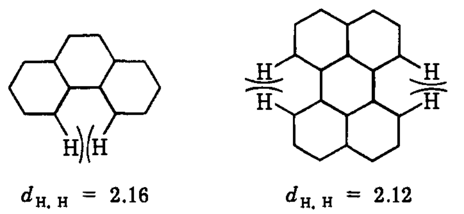
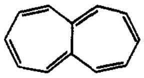
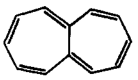


Figure 2. Hydrogen overcrowding in planar aromatic hydrocarbons.

The experimental structures listed in Table V indicate this is the case and our calculated lengths for these bonds are reasonable. The central bond, however, is calculated to be considerably shorter than what has been observed.

An interesting comparison with azulene is bicyclo[5.5.0]dodecahexaene. Although this compound has been prepared, little is known about it since it is stable only in dilute solution in the cold.[35] Such unstable compounds are a prime target for structure determinations by means of calculational methods. The compound is expected to be nonaromatic even though its Kekulé forms indicate bond regularity, because the Hückel ($4n + 2$) condition is not satisfied.





Our calculations (assuming C_{2h} symmetry) find bond alternation with lengths ranging between 1.355 and 1.481 Å (Table VI). Additional support for this structure is the earlier finding[36] that the experimental uv spectrum is best explained in terms of a planar structure with strong bond alternation.

The conformation of biphenyl has been reported as

---

(32) G. Dallinga, P. J. Smit, and E. L. Mackor in "Steric Effects in Conjugated Systems," G. W. Gray, Ed., Butterworths, London, 1958, p 150.

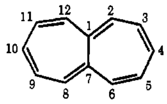
(33) C. A. Coulson, *J. Chem. Soc.*, 2775 (1962).

(34) C. A. Coulson and C. W. Haigh, *Tetrahedron*, **19**, 527 (1963).

(35) H. J. Dauben, Jr., and D. J. Bertelli, *J. Amer. Chem. Soc.*, **83**, 4657 (1961).

(36) N. L. Allinger, M. A. Miller, L. W. Chow, R. A. Ford, and J. C. Graham, *J. Amer. Chem. Soc.*, **87**, 3430 (1965), and references therein.

Table VI. Calculated Geometry of Bicyclo[5.5.0]dodecahexaene



Bond	Length, Å	Bond	Length, Å
1–2	1.378	5–6	1.357
2–3	1.453	6–7	1.481
3–4	1.355	1–7	1.480
4–5	1.448		

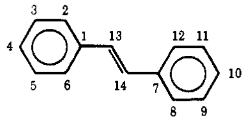
planar in the crystal[37–39] but nonplanar in the gas phase.[40] In the planar form, H···H nonbonded interactions of the type found in phenanthrene (Figure 2) are present, and Bastiansen and Traettberg[41] have suggested that this is the cause of the nonplanarity in the gas phase. Various bond order–bond length methods applied to biphenyl have invariably underestimated the central bond length, since they have not accounted for these H···H interactions in the planar form. This problem was not very apparent in the compounds shown in Figure 2 since, unlike biphenyl, they have only one interaction per "peri" bond and the effect is small. Fischer-Hjalmars[20] investigated the suggestion of Bastiansen by calculating the total C_{sp^2}–C_{sp^2} rotational potential in biphenyl as the sum of the conjugation energy and H···H interaction energy as a function of the dihedral angle, ω, between the rings. The conjugation energy was obtained from a modified Pariser–Parr–Pople method and the nonbonded interactions were calculated with functions suggested by Bartell.[42] Our model, as applied to biphenyl, is essentially the same type of calculation except that a more sophisticated force field is used, and the energy of the molecule is allowed to minimize in all other degrees of freedom during the rotation. Our results differ but little from those of Fischer-Hjalmars. The gas phase value[41] for the inclination of the rings with respect to one another is 41.6°. Our calculated value is higher, approximately 50°, with a large amplitude of oscillation. The planar conformation found in crystals is a result of the intermolecular interactions being larger than the modest intramolecular potential. Since the planar conformation should give more favorable packing, it is reasonable for biphenyl to exist in the crystal in this form. Our calculated length for the central bond is 1.490 (planar) and 1.487 (ω 50°), in agreement with the X-ray value (planar) of 1.497 Å.[39]

The barrier to rotation in biphenyl is less than 5 kcal/mol and is due primarily to nonbonded interactions between the ortho hydrogens in the planar form. We find that replacing one of these four hydrogens with a methyl group will increase the E_{ster} for the planar conformation by about 5 kcal/mol and thus cause E_{tot} to have its minimum at 90°. This is compatible with the conclusions drawn from electronic spectra, that a single *o*-methyl group has a significant effect on the intensity and location of the biphenyl conjugation band,[43] and it qualitatively supports the findings of optical studies that ortho,ortho′-disubstituted biphenyls can have barriers of 20–40 kcal/mol.[44]

Styrene has been studied and, as one might expect, displays many of the features found in biphenyl. The planar form has a "phenanthrene-type" H···H interaction which is relieved by rotation of the vinyl group about the C_{sp^2}–C_{sp^2} single bond. Although its π-bond order is a little larger than the analogous biphenyl linkage ($p_{1,7}$ = 0.28 for styrene and 0.26 for biphenyl), the gas-phase conformation is expected to be less distorted from planarity than is biphenyl since styrene has only one H···H interaction in the planar form. Our calculations find that a nonplanar form ($\omega \sim 37°$) is at the minimum of an extremely shallow rotational potential, being favored over the planar form by only 0.5 kcal/mol and over the 90° form by 1.45 kcal/mol. No experimental data on styrene appear to be available for comparison.

The conjugation energy is essentially the same in butadiene, styrene, and biphenyl, and the relative magnitudes of the steric interactions determine the three different minimum energy conformations. In butadiene, the relatively small steric potential is dominated by the conjugation energy and the two planar forms (s-cis and s-trans) are at energy minima. The steric potential for biphenyl, however, is larger than in butadiene because of the rather high rigidity of the ring and the inability of the interacting ortho hydrogens to bend back away from one another. This steric energy in biphenyl is of sufficient magnitude that the planar form is an energy maximum, destabilized even with respect to the 90° conformation. Styrene represents an intermediate case where the conjugation and steric potentials are about equal. The result is a very shallow composite curve with an energy minimum between the planar and 90° forms.

trans-Stilbene has the same kind of shallow C_{sp^2}–C_{sp^2} single bond rotational potential as was found with styrene, except that the bond order of the C_1–C_{13} bond is large enough ($P_{1,13}$ = 0.30) to shift the energy minimum to the planar conformation by increasing the conjugation energy from 4.6 kcal/mol (styrene) to 5.2 kcal/mol (stilbene).



Our calculated barrier to rotation about the central C_{sp^2}–C_{sp^2} double bond (p = 0.91) is 43.5 kcal/mol as compared with an experimental value of 43 kcal/mol.[23] A recent CNDO/2 study of stilbene[45] has found the energy indifference to phenyl rotation indicated in our calculations, but has produced an unreasonable 129 kcal/mol barrier to rotation about the central bond. The error is probably due to the lowest energy configuration being a poor representation of the lowest

---

[37] H. Hargreaves and S. HasanRizvi, *Acta Crystallogr.*, **15**, 365 (1962).

[38] J. Trotter, *Acta Crystallogr.*, **14**, 1135 (1961).

[39] G. B. Robertson, *Nature (London)*, **191**, 593 (1961).

[40] A. Almenningen and O. Bastiansen, *Kgl. Nor. Vidensk. Selsk. Skr.*, No. 4, 1 (1958).

[41] O. Bastiansen and M. Traetteberg, *Tetrahedron*, **17**, 147 (1962).

[42] L. S. Bartell, *J. Chem. Phys.*, **32**, 827 (1960).

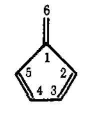
[43] G. H. Beaven in "Steric Effects in Conjugated Systems," G. W. Gray, Ed., Academic Press, New York, N. Y., 1958, p 22.

[44] F. H. Westheimer in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, p 523.

[45] S. Ljunggren and G. Wettermark, *Theor. Chim. Acta*, **19**, 326 (1970).

electronic state in the perpendicular geometry, as has been found to be the case for ethylene.[46]

Fulvene is a nonbenenzoid molecule which one might expect to display strong bond alternation. Experimental data are very scanty for this molecule, primarily due to its extreme reactivity. An electron diffraction geometry[47] is available, although in view of its assumptions made, the structure may be quite inaccurate. It has, in fact, been found to give the wrong rotational constants to account for the microwave spectrum.[48] The electron diffraction structure of dimethylfulvene[49] shows significantly shorter C_{sp^2}–C_{sp^2} bonds than were found for fulvene itself. A comparison of these structures with our calculated results is shown in Table VII. The calculated bond lengths are in marginal agreement with the experimental values. Keeping in mind the problems and the assumptions used in deducing the experimental fulvene structure, we feel that the geometry of the C_{sp^2} system is quite similar in fulvene and dimethylfulvene, and that our structure is at least as reliable as any other. From the viewpoint of π-electron delocalizations, our results agree with the conclusions of other theoretical studies[50] that the molecule is not aromatic and should display the characteristics of cyclic polyolefins.



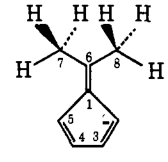


Table VII. Experimental and Calculated Fulvene Structures

	Fulvene		Dimethylvulfene	
	ED[a]	Calcd	ED[b]	Calcd
		Bond, Å		
1–2	1.496	1.457	1.476 ± 0.008	1.455
2–3	1.382	1.354	1.340 ± 0.006	1.357
3–4	1.496	1.446	1.462 ± 0.009	1.438
1–6	1.382	1.355	1.347 ± 0.010	1.369
6–7			1.510 ± 0.010	1.514
		Angle, deg		
5–1–2	106.5	106.6	(106)	105.7
1–2–3	107.8	107.5	(108)	108.2
2–3–4	109.0	109.2	109.0 ± 1.2	109.0

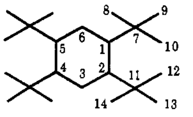
[a] Reference 47. [b] Reference 49.

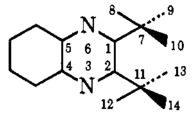
Experimental structural data concerning severe steric interactions on conjugated systems are important to us as they provide a good test of the combined σ–π functions of our force field. We have calculated the effects of the mutual repulsion of the *t*-butyl groups in *o*-di-*tert*-butylbenzene and found favorable agreement (Table VIII) with the reported crystal structures of 1,2,4,5-tetra-*tert*-butylbenzene[51] and *o*-di-*tert*-butylquinoxaline.[52] The conformations of the *t*-butyl groups in these molecules are probably quite dependent on the crystal packing and need not agree with the calculated conformations of *o*-di-*tert*-butylbenzene shown.

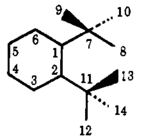
Table VIII. Structure of Some *o*-Di-*tert*-butylbenzene Derivatives

	Tetra-*tert*-butylbenzene X-Ray[a,b]	Di-*tert*-quinoxaline X-Ray[c]	Di-*tert*-benzene Calcd
		Bond, Å	
1–2	1.416	1.457	1.427
2–3	1.395–1.398		1.402–1.405
1–7	1.566–1.568	1.555	1.539–1.566
7–8	1.49–1.57	1.533–1.550	1.546–1.559
		Angle, deg	
1–2–3	115.1–115.4	118.7	114.8–118.9
7–1–2	129.9–131.0	129.8	126.5–132.8
1–7–8	110–116	113–116	107.0–124.7

[a] The calculated positional standard deviations for the ring atoms and adjacent atoms are 0.005 and 0.006 Å, respectively. [b] Reference 51 [c] Reference 52.







A twisted form of *o*-di-*tert*-butylbenzene was also studied in view of our results with *cis*-di-*tert*-butylethylene,[7] but the calculated energy was higher than for the regular planar form. This is in agreement with the quinoxaline study which found atoms 1, 2, 7, and 11 to be coplanar. We do expect, however, some correlation of bond lengths and bond angles. An examination of Table VIII shows reasonable agreement between the structures, the main exception being the 0.03 Å longer C_1–C_2 bond length of the quinoxaline ring. (The corresponding bond in napthalene is 0.015 Å longer than the benzene bond length, however.)

The minimum energy forms of several conjugated cyclic dienes were calculated since these molecules are components of larger molecules which are of chemical and biological interest. The simplest of these cyclenes is 1,3-cyclopentadiene. Conjugation across bond c favors planarity of the π system, the staggered relation between the methylene hydrogens and the vicinal hydrogens discourages envelope distortions (due to unfavorable propene-type torsional interactions), and the sum of the "natural valence angles" is greater than the total of interior angles of a pentagon, a factor which again favors planarity. Thus the C_{sp^2}–C_{sp^3} bonds appropriate to butadiene and the C_{sp^2}–C_{sp^2} bond of propene are good approximations to the ring geometry. Several experimental structures are compared with our calculated geometry in Table IX, and the agreement is good.

It has been suggested by Beckett and Mulley[53] on the basis of chemical arguments that the 1,3-cyclohexadiene ring in 9,10-dihydrophenanthrene is nonplanar. A semiquantitative estimate of the degree of nonplanarity in the cyclohexadiene itself was made by Butcher[54] from an analysis of the ground vibrational state rotational constants. Assuming C_{sp^2}–C_{sp^2} bond lengths of 1.34 and 1.47 Å and all other C–C lengths

---

(46) U. Kaldor and I. Shavitt, *J. Chem. Phys.*, **48**, 191 (1968).

(47) M. Rouault and Z. L. Waziutynska, *Acta Crystallogr.*, **10**, 804 (1957).

(48) R. D. Brown, F. R. Burden, and J. E. Kent, *J. Chem. Phys.*, **49**, 5542 (1968).

(49) J. F. Chiang and S. H. Bauer, *J. Amer. Chem. Soc.*, **92**, 261 (1970).

(50) T. Nakajima and S. Katagiri, *Mol. Phys.*, **7**, 149 (1963).

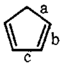
(51) A. van Bruijnsvoort, L. Eilermann, H. van der Meer, and C. H. Stam, *Tetrahedron Lett.*, (1968), 2527.

(52) G. J. Visser, A. Vos, A. de Groot, and H. Wynberg, *J. Amer. Chem. Soc.*, **90**, 3253 (1968).

(53) A. H. Beckett and B. A. Mulley, *Chem. Ind.* (*London*), 146 (1955).

(54) S. S. Butcher, *J. Chem. Phys.*, **42**, 1830 (1965).

Table IX. Cyclopentadiene Geometry



	X-Ray[a,b]	Microwave[b,c]	Calcd
		Bond, A	
a	1.48 1.51	1.509 ± 0.002	1.506
b	1.27 1.37	1.342 ± 0.002	1.342
c	1.44	1.469 ± 0.002	1.458
		Angle, deg	
a–b	108 110	109.3 ± 0.2	110.6
b–c	112 107	109.4 ± 0.2	108.8
a–a	102	102.8 ± 0.2	101.1

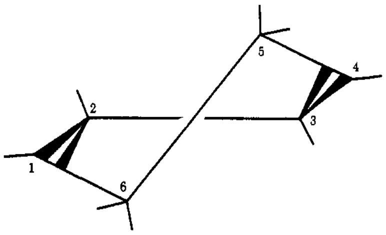
[a] ±0.04 Å. [b] G. Liebling and R. Marsh, *Acta Crystallogr.*, **19**, 202 (1965). [c] These are r_0 values. [d] L. H. Scharpen and V. W. Laurie, *J. Chem. Phys.*, **43**, 2765 (1965).

Table X. Experimental and Theoretical Structures of 1,3-Cyclohexadiene

	Electron diffraction geometries			Theoretical geometries	
	Dallinga and Toneman[b]	Traetteberg[c]	Oberhammer and Bauer[d]	Favini, *et al.*[e]	Calcd
		Bond, Å			
1–2	1.339 ± 0.001	1.348 ± 0.001	1.350 ± 0.004	1.331[a]	1.345
2–3	1.468 ± 0.008	1.465 ± 0.002	1.468 ± 0.014	1.477[a]	1.461
1–6	1.494 ± 0.017	1.519 ± 0.001	1.523 ± 0.016		1.508
5–6	1.510 ± 0.032	1.538 ± 0.003	1.534 ± 0.020		1.532
		Angle, deg			
1–2–3	121.6 ± 1.0	120.26 ± 23	120.1 ± 0.6	120.0	120.5
2–1–6	118.2 ± 0.7	120.25	120.1 ± 0.5	120.7	121.3
4–5–6	111.5 ± 0.5	110.88	110.7	111.1	112.3
ω 1–2–3–4	17	18	18.3	17.5	12

[a] Assumed length. [b] Reference 57. [c] Reference 58. [d] Reference 59. [e] Reference 56.

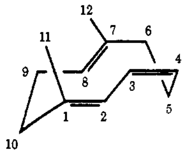
as 1.50 Å, he deduced a torsional angle, ω (the angle by which one ethylene group is rotated relative to the other about the C_2–C_3 bond), of 17.5 ± 2°. Favini and coworkers[55] have recently studied medium ring olefins and have subsequently extended it to cycloalkadienes[56] by making the C_{sp^2}–C_{sp^2} bond length a function of the dihedral angle, and the dihedral angle a function of the π–π resonance integral. While their bond length relationships are quite similar to the popular bond order–bond length relationships mentioned previously, they have the disadvantage that a new function is required for every type of C_{sp^2}–C_{sp^2} bond.



1,3-cyclohexadiene

Pertinent experimental[57–59] and theoretical structures for 1,3-cyclohexadiene are listed in Table X. The only noteworthy discrepancies between our structure and the others listed are the mutually dependent C_4–C_5–C_6 bond angle and the C_1–C_2–C_3–C_4 dihedral angle. Traetteberg[58] has commented that possible distortion about the ethylene C_{sp^2}=C_{sp^2} bonds cannot be ruled out (we calculated them twisted about 2°) and that the dihedral angle may be smaller than reported. The calculated potential energy surface in the vicinity of the ω = 12° conformation is rather shallow, and a wide amplitude of vibration is expected, which tends to make comparison with experiment difficult. The nonplanarity of the ring itself is very likely due to two factors: the nonbonded interactions of the methylene protons at C_5 with those at C_6 (they are eclipsed in the planar conformation) and the angle strain which would exist in the planar form due to the two tetrahedral ring carbons. Factors opposing nonplanarity are the nonbonded interactions of the methylene protons with the vinyl protons at C_1 and C_4 and the disruption of the π system as the ethylene groups are rotated relative to one another across the C_2–C_3 bond.

Pregeijerene, a natural-product hydrocarbon, is a monocyclic polyolefin containing a conjugated diene linkage. We were prompted to investigate its geometry because of the interesting features revealed in a recent X-ray study[60] of the silver nitrate adduct. The basic ring structure is shown with the silver ion complexed only with the diene linkage (the numbering system used is for convenience in our calculations). As discussed earlier,[7] the isolated double bond has rehybridized rather than simply twisted in order to relieve ring strain, a distortion which our calculations have duplicated reasonably well. The trisubstituted linkage in the diene moiety displays this rehybridization to an even greater extent, but our calculations are no longer in good agreement (see Figure 3). This may be due to the fact that the silver ion complexed with the 1–2–3–4 linkage is associated with the conjugated diene linkage



pregeijerene conformation in the crystal

---

(55) G. Favini, G. Buemi, and M. Raimondi, *J. Mol. Struct.*, **2**, 137 (1968).

(56) G. Favini, F. Zuccarello, and G. Buemi, *J. Mol. Struct.*, **3**, 385 (1969).

(57) G. Dallinga and L. H. Toneman, *J. Mol. Struct.*, **1**, 11 (1967).

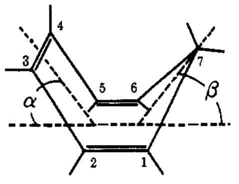
(58) M. Traetteberg, *Acta Chem. Scand.*, **22**, 2305 (1968).

(59) O. Oberhammer and S. Bauer, *J. Amer. Chem. Soc.*, **91**, 10 (1969).

(60) P. Coggon, A. T. McPhail, and G. A. Sim, *J. Chem. Soc. B*, 1024 (1970).

in the silver nitrate adduct[60] and consequently the π bonds should be noticeably weakened and thus subject to a greater distortion than an uncomplexed linkage. It might be noted that our calculated dihedral angle across the C_{sp^2}–C_{sp^2} single bond of 127.0° coincides with the reported value of 128.6°.

A nonplanar structure[61] for cycloheptatriene has been established, but conflicting results concerning the degree of nonplanarity have been published.[62,63] The quantitative estimate made by Butcher[62] from the rotational constants of the normal isotopic species (no detailed structural information could be obtained directly from the spectroscopic data) was determined by assuming bond lengths and angles, thus determining the angles α and β. He found these angles to be somewhat insensitive to the choice of bond lengths and angles and thus presumed them to be quite accurate. His values are: α = 29.5 ± 4° and β = 50 ± 5°. Traetteberg[63] determined the total molecular structure by electron diffraction and found α = 40.5 ± 2° and β = 36.5 ± 2°. Our results, listed in Table XI, agree pretty well with Butcher's estimates.

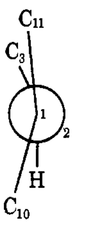


1,3,5-cycloheptatriene

Table XI. Geometry of 1,3,5-Cycloheptatriene

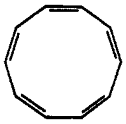
	Butcher[b]	Traetteberg[c]	Calcd
		Bond, Å	
1–2	1.34[a]	1.356 ± 0.005	1.348
2–3	1.47[a]	1.446 ± 0.007	1.463
3–4	1.34[a]		1.356
1–7	1.50[a]	1.505 ± 0.007	1.504
		Angle, deg	
1–2–3	124.5	127.2	124.8
1–2–3	124.5	127.2	124.8
2–3–4	124.5	119.8	126.1
2–1–7	124.5	121.8	122.2
1–7–6	105		112.2
α	29.5 ± 4	40.5 ± 2	28
β	50 ± 5	36.5 ± 2	49.5

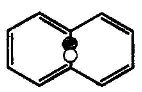
[c] Assumed value. [b] Reference 62. [c] Reference 63.



	Calcd	*Exptl*
$\omega_{10\text{-}1\text{-}2\text{-}3}$	162.5°	150.4°
$\omega_{11\text{-}1\text{-}2\text{-}3}$	6.3°	10°
$\omega_{10\text{-}1\text{-}2\text{-}H}$	9.8°	

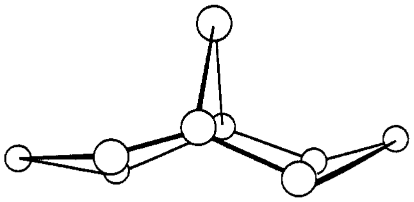
Figure 3. Geometry across the C_1=C_2 bond in pregeijerene.



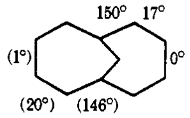


A number of annulenes have been studied in the current work, and we will first discuss cyclodecapentaene. In view of the geometrical problems indicated by models, it is hardly surprising that the compound was not isolated until 1971.[64] Planar forms of cyclodecapentaene, predicted to be aromatic by Hückel's rule (4n + 2), are prohibited either by angle strain (all cis) or transannular H···H repulsions (3 cis, 2 trans). Simple distortions from these structures to relieve this strain are calculated to result in very unfavorable π systems. Theoretical interest in the aromatic character of this ten-membered ring encouraged the synthesis of related molecules[65] in which the overcrowded hydrogens of 3 cis, 2 trans have been replaced by various bridging groups. The methylene bridged compound, bicyclo[4.4.1]undecapentaene, is found to be nonaromatic in the chemical sense, although the ultraviolet spectrum suggests extensive conjugation. The nmr spectrum shows eight protons at τ 7.5–6.8 and two protons at τ −0.5, which may be considered as evidence for a ring current.[65]

An X-ray examination[66] of a crystalline carboxybicyclo[4.4.1]undecapentaene indicates a relatively planar structure with outer ring bond lengths constant (to approximately within experimental error). This is less than the difference found in the peripheral bonds of naphthalene (0.05 Å), and suggests considerable aromatic character. Our calculated geometry (assumed C_{2v}) is in good agreement with the X-ray structure as shown in Table XII. The dihedral angles in the ten-membered ring are distorted no more than 30° from planarity, with the average distortion being only 19° (the average experimental values (average deviation about 2°) are given in parentheses).

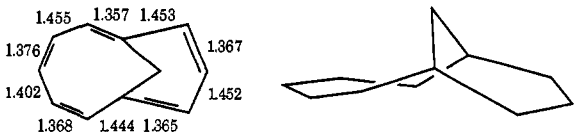


bicyclo[4.4.1]undecapentaene



ring dihedral angles in bicyclo[4.4.1]undecapentaene

The less symmetrical (unknown) isomer of this compound, bicyclo[5.3.1]undecapentaene, has a 1,5 methylene bridge and is calculated to have complete bond alternation. The lack of aromaticity is a consequence



calculated bond lengths in bicyclo[5.3.1]undecapentaene

---

(61) F. R. Jensen and L. A. Smith, *J. Amer. Chem. Soc.*, **86**, 956 (1964).

(62) S. S. Butcher, *J. Chem. Phys.*, **42**, 1833 (1965).

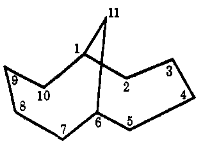
(63) M. Traetteberg, *J. Amer. Chem. Soc.*, **86**, 4265 (1964).

(64) S. Masamune, K. Hojo, G. Bigam, and D. L. Rabenstein, *J. Amer. Chem. Soc.*, **93**, 4966 (1971).

(65) E. Vogel and H. D. Roth, *Angew. Chem., Int. Ed. Engl.*, **3**, 228 (1964).

(66) M. Dobler and J. D. Dunitz, *Helv. Chim. Acta*, **48**, 1429 (1965).

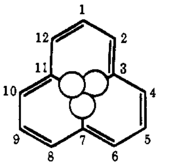
Table XII. Geometry of Bicyclo[4.4.1]undecapentaene



	X-Ray[a,b]	Calcd
	Bond, Å	
1-2	1.409	1.406
2-3	1.383	1.400
3-4	1.414	1.423
1-11	1.477	1.470
	Angle, deg	
1-11-6	99.6	99.1
2-1-11	116.1	115.8
1-2-3	122.3	120.4
2-3-4	127.7	128.6

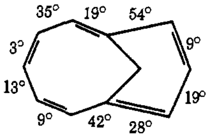
[a] Average values. Reported results show bond lengths nonequivalent by 0.01 Å and angles by 2°. Standard deviations are 0.01 Å and 0.3°. [b] Reference 66.

Table XIII. Calculated Geometry of [12]Annulene



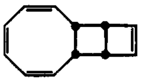
Bond	Length, Å	Angle	Deg	Angle	Deg
1-2	1.515	12-1-2-3	74.0	1-2-3	120.1
2-3	1.337	1-2-3-4	174.1	2-3-4	122.6
3-4	1.516	2-3-4-5	90.2	3-4-5	124.2
4-5	1.348	3-4-5-6	0.4	4-5-6	126.4
5-6	1.474	4-5-6-7	36.3	5-6-7	125.1
6-7	1.350	5-6-7-8	176.3	6-7-8	123.9
7-8	1.475	6-7-8-9	138.0	7-8-9	121.7
8-9	1.352	7-8-9-10	5.5	8-9-10	121.9
9-10	1.474	8-9-10-11	45.2	9-10-11	120.4
10-11	1.349	9-10-11-12	174.6	10-11-12	125.2
11-12	1.470	10-11-12-1	145.0	11-12-1	119.7
12-1	1.346	11-12-1-2	3.5	12-1-2	119.8

of σ system constraints which forces several ring dihedral angles to differ up to 54° from planarity, with an average distortion of 23°, effectively generating a π system composed of isolated segments, each with an even number of π atomic centers. This compound is thus fundamentally quite different from the isomeric [4.4.1] system, even though their average planarities are similar.

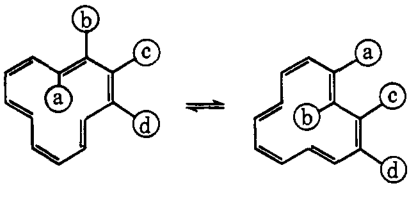


torsional angles in bicyclo[5.3.1]undecapentaene

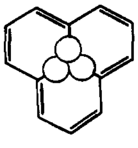
Larger completely conjugated ring systems have long been of theoretical interest because of their relation to Hückel's $(4n + 2)$ rule.[67] The next of these is [12]-annulene which has been postulated[68,69] as a primary product of the photolysis of *syn*-tricyclo[8.2.0.0^{2,9}]-dodeca-3,5,7,11-tetraene.



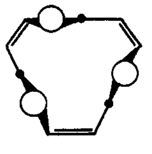
The nmr spectrum of the compound has been interpreted as the rapidly interconverting conformation shown, and shows no evidence for aromaticity.



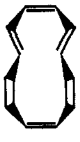
The internal hydrogens (δ −0.56) are rather strongly deshielded owing to their being jammed into the induced fields of nearby double bonds. At increased temperature, the δ 1.34 quartet is quite normal for an olefin and the δ 0.43 quartet is a reasonable average for a proton spending half its time in the interior of the ring. This conformation was predicted to have 50–60° torsional angles about the C_{sp^2}–C_{sp^2} single bonds on the basis of models. The activation enthalpy for the interconversion was deduced *via* nmr to be 3.7 ± 0.2 kcal/mol, and **2** was suggested as the transition state. Our calculations find **1** to be the most stable of several possible conformations (**1**–**3**), with torsional angles across the C_{sp^2}–C_{sp^2} single bonds deviating 35–90° from planarity (see Table XIII). This nonplanarity is the result of the internal H···H repulsions. It might be noted that while the three internal hydrogens are not equivalent, they are able to exchange with one another faster than **1** is able to interconvert, and thus appear equivalent, Replacing these hydrogens with a methine bridge results in a molecule (**4**) which has ring



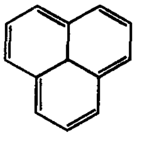
1



2



3



4

---

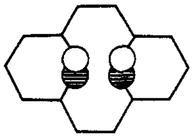
(67) F. Sondheimer and R. Wolovsky, *J. Amer. Chem. Soc.*, **84**, 260 (1962).

(68) J. F. M. Oth, H. Rottele, and G. Schroder, *Tetrahedron Lett.*, 61 (1970).

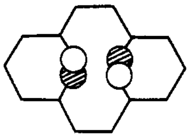
(69) J. F. M. Oth, J. M. Gilles, and G. Schroder, *ibid.*, 67 (1970).

torsional angles deviating less than 15° from planarity and a bond alternation of 1.356–1.460 Å. Structure **2** is calculated to have an energy of 3.3 kcal/mol above **1**, which is consistent with the experimental ΔH^* for interconversion. Structure **2** is not an unambiguous transition state, however. Structure **3**, with a relative conformational energy of 2.1 kcal/mol, was discounted as a possible transition state or intermediate since it is a structural isomer with one less trans double bond than **1**, and considerable energy would be required to interconvert it.

The compound [14]annulene is one of a series of annulenes studied by Sondheimer.[70] Its room temperature nmr spectrum was found[71] to consist of two sharp singlets at δ 5.58 and 6.07 in a ratio of about 6:1. This has been attributed[72] to the existence of two conformational isomers, **5** and **6**.



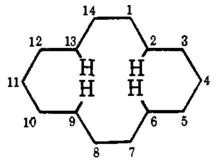
5(C_{2h})



6(D_2)

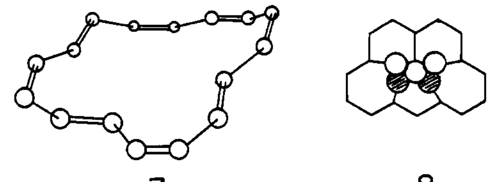
An X-ray examination[73] of the crystalline state indicates that unless there is disorder in the crystal, the molecules are centrosymmetric; thus, **5** is presumed the more stable isomer. Our calculations (Table XIV) support this interpretation, indicating **5** is 2.5 kcal/mol more stable than **6**.

Table XIV. [14]Annulene Calculated Geometry



	C_{2h}	D_2
	Bond, Å	
1–14	1.410	1.407
1–2	1.408	1.409
2–3	1.405	1.403
3–4	1.411	1.413
	Angle, deg	
14–1–2	124.2	120.4
1–2–3	126.9	130.3
2–3–4	123.7	125.2
3–4–5	126.9	129.7
2–1–14–13	0	23.5
14–1–2–3	158.5	158.1
1–2–3–4	163.4	174.5
2–3–4–5	18.7	15.1

The energy difference between these conformations is due primarily to the ring distortions caused by the internal hydrogen repulsions. In **5** the ring undergoes torsional deformations with an average deviation from planarity of 16.2° and bond angle deformations with an average ring angle of 125.2°. In **6** the ring is more planar (12.6° average deviation from planarity), but the average ring angle is expanded to 125.9°. The result is that while **5** has 0.4 kcal/mol more torsional energy and 0.8 kcal/mol more van der Waals repulsions than **6**, the latter is destabilized by its 3.3 kcal/mol greater bending energy.

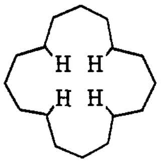


7 8

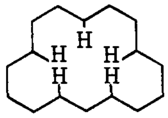
Figure 4. Conformations of [16]annulene.

The aromatic character of this molecule is indicated in the unusual low temperature nmr spectrum of **5**,[74] in which the outer protons appear at low field (δ 7.6) and the inner protons appear at very high field (δ 0.0). The regular bond lengths of our calculated structure, listed in Table XIV, support this interpretation.

The compound [16]annulene[75] is predicted to be nonaromatic by Hückel's rule and should thus exhibit bond alternation, with the resulting butadiene-type single bonds giving the ring considerable flexibility. Older low temperature nmr studies[76] indicated the lack of aromatic protons, and more recent measurements[77] have suggested that at room temperature the equilibrium mixture exists of structures similar to **7** and **8** in a ratio of about 7:3.



7



8

The crystal structure of [16]annulene,[78] determined by two independent groups, shows the molecule to be nonplanar with almost complete bond alternation (1.454 Å, 1.333 Å). The average torsional angle across s-cis C_{sp^2}–C_{sp^2} single bonds is 41° and the molecule has approximate S_4 symmetry (see Figure 4 and Table XV). Our calculated S_4 structure is in good agreement with experiment (see Table XV) except for the 57° torsional angle across the s-cis bonds. As was evidenced in biphenyl, however, a certain amount of flattening is expected in the crystal and we therefore have confidence in our gas phase geometry. As a result of the flattening, the crystal structure also displays smaller (1–4°) bond angles.

Our calculated structure corresponding to **8** is shown in Figure 4 and has bond alternation (1.365–1.460 Å) and nonplanarity to about the same extent as was found for **7**. Due to more severe nonbonded interactions, it is calculated to be 7.23 kcal/mol less

---

[70] F. Sondheimer and Y. Gaoni, *J. Amer. Chem. Soc.*, **82**, 5765 (1960).

[71] L. M. Jackman, F. Sondheimer, Y. Amiel, D. A. Ben-Efraim, Y. Gaoni, R. Wolovsky, and A. A. Bothner-By, *J. Amer. Chem. Soc.*, **84**, 4307 (1962).

[72] Y. Gaoni and F. Sondheimer, *Proc. Chem. Soc. London*, 299 (1964).

[73] J. Bregman, *Nature (London)*, **194**, 679 (1962).

[74] F. Sondheimer, *Proc. Roy. Soc., Ser. A*, **297**, 173 (1967).

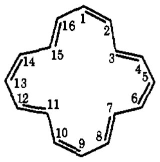
[75] F. Sondheimer and Y. Gaoni, *J. Amer. Chem. Soc.*, **83**, 4863 (1961).

[76] G. Schroder and J. F. M. Oth, *Tetrahedron Lett.*, 4083 (1966).

[77] J. F. M. Oth and J. M. Gilles, *Tetrahedron Lett.*, 6259 (1968).

[78] S. M. Johnson, I. C. Paul, and G. S. D. King, *J. Chem. Soc. B*, 643 (1970).

Table XV. Geometry of [16]Annulene



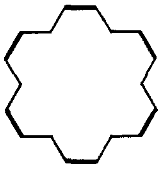
	Exptl[a]	Calcd[a]
	Bond, Å	
1–2	(1.312–1.338) ± 0.012	1.352
2–3	(1.443–1.470) ± 0.012	1.465
3–4	(1.326–1.352) ± 0.012	1.350
4–5	(1.442–1.470) ± 0.012	1.484
	Angle, deg	
1–2–3	(125.9–128.2) ± 0.8	124.9
2–3–4	(121.1–122.8) ± 0.7	122.6
3–4–5	(126.2–127.2) ± 0.6	123.0
3–4–6	(127.9–129.6) ± 0.8	124.9
16–1–2–3	2–7	1.8
1–2–3–4	175–180	176.8
2–3–4–5	174–177	178.4
3–4–5–6	37–42	57.1

[a] Approximate D_4 symmetry assumed.

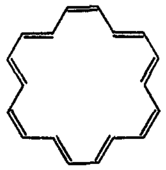
stable than the S_4 form. This number is not compatible with the nmr results, and indicates that our calculated nonsymmetrical structure is not the one they are referring to. The problem is that a large variety of structures can fit the nonsymmetrical requirements (the simplicity of the drawing is very misleading) and when the spectroscopists speak of a structure "such as 7," they might more properly say "an unknown irregular conformation."

Probably the most thoroughly studied molecule of this series is [18]annulene, even though considerable ambiguity still exists regarding its structure and the factors affecting its stability. A structure of equal bond lengths, as originally predicted[79] by simple bond order calculations, now turns out upon a reexamination from the valence bond point of view to be a saddle point.[80] These large cyclic polyenes ($C_{2n}H_{2n}$) are predicted to tend toward bond alternation as n increases as a result of the influence of the σ-compression energy. This is in agreement with the results of MO theory,[81] which demonstrates that alternation must occur as $n \rightarrow \infty$. Although the theories disagree slightly as to when alternation sets in, both indicate that it will occur in [18]annulene. Experimental evidence, however, seems to contradict the alternation theory. The slightly distorted D_{6h} molecular symmetry found in the crystal structure (**9**)[82] is claimed to rule out alternate long and short bonds and instead shows a different type of distortion: 12 inner (trans) bonds (shown light in **9**) of mean length 1.382 ± 0.003 Å and six outer (cis) bonds (dark in **9**) of mean length 1.419 ± 0.004 Å, with ring carbon atom deviations of ±0.085 Å from the mean plane of the ring. Using this geometry in a PPP calculation,[83] errors up to 1.0 eV were encountered in certain transition energies, which led the investigators to conclude that the molecule does not have this structure in solution. They found instead that a bond alternated structure ($\Delta l \approx$ 0.08 Å) of D_{3h} symmetry better fits the observed electronic spectrum and suggested that a small amount of nonplanarity (D_3) might further improve the agreement.

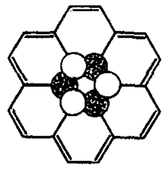
We have calculated minimum energy structures corresponding to these symmetries, plus D_6 (nonplanar), and it was found that the D_3 structure (**11**) is favored over D_{3h} by 8.89 kcal/mol and over D_{6h} by 10.15 kcal/mol. The mean nonplanarity of the carbon atoms of our calculated D_6 structure is only ±0.036 Å, with a 1.90 kcal/mol stabilization in respect to the D_{6h}.



9
D_{6h} crystal



10
D_{3h}
planar-alternant



11
D_3
nonplanar-alternant

The most stable calculated structure (**11**) has a mean nonplanarity of 0.102 Å for the carbons (see Table XVI for the complete geometry), and, as suggested[83] this structure has led to an even better fit between the calculated and experimental uv spectra.[84] The particular puckering arrangement of the carbons in the D_3 structure permits the inner hydrogens to move ±0.568 Å out of the plane, and increases the distance between the adjacent ones from 1.99 Å in the D_{3h} structure to 2.22 Å in the D_3 structure.

Table XVI. Calculated Geometry of [18]Annulene (D_3)

Bond	Calcd length	Angle	Calcd angle	Atom	Displacement from mean plane, Å
1–2	1.357	18–1–2	122.7	1	0.062
2–3	1.463	1–2–3	125.7	2	−0.186
3–4	1.361	2–3–4	123.4	3	−0.058
4–5	1.463	3–4–5	123.4	4	0.058
5–6	1.357	4–5–6	125.7	5	0.186
6–7	1.467	5–6–7	123.0	6	−0.062

We have no reason to believe that the structure we calculate for [18]annulene (D_3) is not correct for the isolated molecule, and the calculations of the electronic spectrum are strong support for our structure. Earlier theoretical studies[85,86] which applied the Pariser–Parr method to the calculation of the electronic spectrum of this compound utilized the X-ray structure, and obtained such poor results that they concluded the Pariser–Parr method was inapplicable here (and by implication, suspect everywhere). We believe the method is applicable here (and in general), but using a wrong structure, one is not likely to calculate the right spectrum.

The problem of the discrepancy between our structure and the X-ray structure remains to be explained. Of the possibilities that come to mind, it may be that

---

(79) C. A. Coulson, *Proc. Roy. Soc., Ser. A*, **169**, 413 (1939).

(80) C. A. Coulson and W. T. Dixon, *Tetrahedron*, **17**, 215 (1962).

(81) H. C. Longuet-Higgins and L. Salem, *Proc. Roy. Soc., Ser. A*, (a) **251**, 172 (1959); (b) **255**, 435 (1960); (c) **257**, 445 (1960).

(82) J. Bregman, F. L. Hirshfeld, D. Rabinovich, and G. M. J. Schmidt, *Acta Crystallogr.*, **19**, 227 (1965).

(83) F. A. Van-Catledge and N. L. Allinger, *J. Amer. Chem. Soc.*, **91**, 2582 (1969).

(84) J. Siefert, unpublished results.

(85) C. Weiss and M. Gouterman, *J. Chem. Phys.*, **43**, 1838 (1965).

(86) N. Trinajstic and R. J. Wratten, *J. Mol. Struct.*, **3**, 395 (1969).

the structure is different in the gas phase and in the crystal. Crystal lattice forces (intermolecular van der Waals forces) are sufficient to flatten out biphenyl (about 5 kcal/mol). To flatten out [18]annulene ($D_3 - D_{3h}$) is calculated to require 8.9 kcal, an amount that might be available. Once the molecule is flat, the D_{3h} structure is favored over the D_{6h} by only 1.16 kcal/mol.

Conclusions

The method formulated here appears to be a convenient adaptation for the application of the force field method to the determination of structures of molecules containing delocalized systems. While previous *ad hoc* calculations have treated many individual systems, each as a special case, this method is general and of wide applicability, as shown by good results with a diversity of structures. The general limitations of force field methods remain.[5,87]

---

(87) J. E. Williams, Jr., P. J. Stang, and P. v. R. Schleyer, *Annu. Rev. Phys. Chem.*, 19, 531 (1968).

Hückel Molecular Orbital π-Resonance Energies. Heterocycles Containing Divalent Sulfur

B. Andes Hess, Jr.,* and L. J. Schaad*

Contribution from the Department of Chemistry, Vanderbilt University,
Nashville, Tennessee 37235. Received December 5, 1972

Abstract: Coulombic and resonance integrals have been evaluated for divalent sulfur from thermodynamic data. These were used in Hückel calculations to obtain resonance energies for a large number of sulfur heterocycles. An excellent correlation between the experimental properties and calculated resonance energies was found for the known compounds.

We have shown that the lack of correlation between Hückel delocalization energies and experimental aromaticity of cyclic conjugated hydrocarbons, especially nonalternant hydrocarbons, is due to an inappropriate choice of reference structure rather than to an inherent fault of the Hückel wave functions.[1] When, in place of isolated double bonds, the reference structure proposed by Dewar[2] in his Pariser–Parr–Pople calculations is used, an excellent correlation between experimental aromaticity and Hückel resonance energies is found for a wide range of cyclic hydrocarbons.[1,3–5] Dewar's reference structure, based on his discovery that the energies of acyclic polyenes are additive, allows the comparison of the calculated π energy of a cyclic compound with the energy of a "localized" cyclic reference structure. The major difference between this "localized" reference structure and the earlier delocalization energy reference is that the contribution of the π part of the carbon–carbon "single" bonds is included in addition to the π contribution of the carbon–carbon double bonds. Hückel π-resonance energies obtained in this manner range from positive (aromatic) to zero (nonaromatic) to negative (antiaromatic).

We have also found that the Hückel method can be used in a very simple manner to calculate heats of atomization accurately for both acyclic and cyclic hydrocarbons.[6] Since the resonance energy of a system equals the difference between its heat of atomization and that of the reference structure,[2,6] this discovery potentially allows the comparison of our calculated resonance energies directly with experimentally determined resonance energies obtained from heats of combustion. Unfortunately, thermochemical data are not yet available for sufficient acyclic polyenes to determine the necessary bond energy terms and to decide whether the π energies of these reference systems are indeed additive.

Recently, we have extended our method of calculation to cyclic systems containing the amine nitrogen, ether oxygen and carbonyl oxygen.[7,8] The results for these are as impressive as those for the hydrocarbons. Sulfur heterocycles show a more varied behavior than their oxygen or nitrogen analogs, and in this paper we present results for conjugated systems containing sulfur atoms each of which donates two electrons to the π system. Predictions will be shown to agree well with observed behavior, including cases where simple rule-of-thumb methods such as counting resonance structures or use of the $4n + 2$ rule fail. In this respect the Hückel method is as least as satisfactory as the more sophisticated Pariser–Parr–Pople work of Dewar and Trinajstić[9] on sulfur heterocycles.

Evaluation of Integrals

Hückel calculations on sulfur heteromolecules require a choice of sulfur atom Coulombic integral (eq 1)

$$\alpha_{S:} = \alpha_C + \beta_{C-C} h_{S:} \qquad (1)$$

---

(1) B. A. Hess, Jr., and L. J. Schaad, *J. Amer. Chem. Soc.*, 93, 305 (1971).

(2) (a) M. J. S. Dewar and C. de Llano, *ibid.*, 91, 789 (1969); (b) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969.

(3) B. A. Hess, Jr., and L. J. Schaad, *Tetrahedron Lett.*, 17 (1971).

(4) B. A. Hess, Jr., and L. J. Schaad, *J. Amer, Chem. Soc.*, 93, 2413 (1971).

(5) B. A. Hess, Jr., and L. J. Schaad, *J. Org. Chem.*, 36, 3418 (1971).

(6) L. J. Schaad and B. A. Hess, Jr., *J. Amer. Chem. Soc.*, 94, 3068 (1972).

(7) B. A. Hess, Jr., L. J. Schaad, and C. W. Holyoke, Jr., *Tetrahedron*, 28, 3657 (1972).

(8) B. A. Hess, Jr., L. J. Schaad, and C. W. Holyoke, Jr., *ibid.*, 28, 5299 (1972).

(9) M. J. S. Dewar and N. Trinajstić, *J. Amer. Chem. Soc.*, 92, 1453 (1970).