system with sweep width calibration obtained by the audio sideband method. Deuterium irradiation was accomplished with an nmr specialities HD-60A decoupler.

**3-Phenylpropanol-1,1-$d_2$.** Reduction of methyl hydrocinnamate with lithium aluminum deuteride in ether in the usual manner afforded the title compound, which was purified by distillation, bp 75-78° (0.7 mm), containing 3% unreacted ester by glpc examination (10% diethylene glycol succinate, 150°).

*threo*-3-Phenylpropanol-1,1,2,3-$d_4$ and -2,3-$d_2$. A solution of 8.1 g (50 mmoles) of methyl cinnamate in 100 ml of ethyl acetate containing 0.103 g of palladium chloride (0.58 mmole) was treated with deuterium gas at 10 psig for 1 hr. The mixture was filtered, the solvent was evaporated at reduced pressure, and methyl *threo*-hydrocinnamate-1,2-$d_2$ was distilled, bp 80-82° (2 mm), homogeneous by glpc (10% silicone oil, 140°). Deuterium analysis[15] showed 14.93 atom % excess deuterium, or 1.79 deuterium atoms/molecule. Reduction of the ester with LiAlD$_4$ and LiAlH$_4$ afforded the $d_4$- and $d_2$-alcohol, respectively.

A 1:1 mixture of *erythro*:*threo*-3-phenylpropanol-1,1,2,3-$d_4$ was prepared[16] by reduction of methyl cinnamate in ether with LiAlD$_4$.

*erythro*-3-Phenylpropanol-1,2-$d_2$. A solution of 40 g (0.30 mole) of 3-phenylpropanal, 94 g (1.0 mole) of isopropenyl acetate, and 3 g of *p*-toluenesulfonic acid was heated under reflux for 22 hr. The cooled solution was diluted with 200 ml of ether, extracted with 100 ml of 10% aqueous potassium hydroxide, two 100-ml portions of 10% aqueous potassium carbonate, and finally with

saturated bicarbonate solution. The dried (K$_2$CO$_3$) ether extracts were concentrated and flash distilled at 0.5 mm, bp 84-100° (0.5 mm). Nmr examination indicated a 2:1 mixture of enol acetate-aldehyde. Fractionation through a concentric tube column afforded a cut of bp 87-89° (1.8 mm), 10.5 g, whose nmr spectrum indicated a 17:1 mixture of *cis-*:*trans*-1-acetoxy-3-phenylpropene, $n^{20.5}$D 1.5153. The nmr spectrum (CCl$_4$) was consistent with the assigned structure and stereochemistry, resonances appearing (Hz from internal TMS) at 125 (s,3,-O$_2$CCH$_3$), 210 (d, 2, $J = 8 \sim 1$ Hz, PhCH$_2$-), 303 (q, 1, $J = 8$, 8 Hz, CH=CHOAc), and 435 (m, 6, C$_6$H$_5$ and CH=CHOAc).

*Anal.* Calcd for C$_{11}$H$_{12}$O$_2$: C, 74.97; H, 6.87. Found: C, 75.17; H, 7.02.

A solution of 5.1 g (29 mmoles) of the above enol acetate was reduced in 150 ml of 2:1 cyclohexane-ethyl acetate with 0.065 g (0.29 mmole) of platinum oxide at 20-psig deuterium pressure. After uptake of gas had ceased (*ca.* 6 hr) the mixture was filtered and solvent was evaporated. The residue was crudely distilled at 1 mm (deuterium analysis, 1.55 deuteriums/molecule) and the distillate saponified by heating under reflux its solution in 60 ml of 10% ethanolic potassium hydroxide for 4 hr. The cooled solution was diluted with water, acidified, and extracted with ether. The dried (MgSO$_4$) ether extracts were concentrated and the residue was distilled, bp 69-70° (1 mm), 2.0 g. Deuterium analysis showed 13.22 atom % excess deuterium, or 1.60 deuteriums/molecule.

(15) Mr. J. Nemeth, Urbana, Ill.
(16) E. I. Snyder, *J. Org. Chem.*, **32**, 3531 (1968).

# Organic Quantum Chemistry. XXI.[1,2] The Structure and Spectrum of Cyclooctadecanonaene ([18]Annulene)[3]

### Frederic A. Van-Catledge[4] and Norman L. Allinger[5]

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**Abstract:** An SCF modification of a previously described version of the semiempirical ASMO-CI method of Pariser and Parr has been applied to the calculation of the π-electronic transitions of a number of unsaturated hydrocarbons. This method generally predicts the electronic transitions to within 0.3 eV of the observed values. This method has been applied to various conceivable structures for the title compound and suggests that the structure best reconciled with the observed spectrum is one having alternating long and short bonds. Energy calculations, which include the compression energy of the σ system and van der Waals' interactions, also indicate that this structure is the favored one. The structure observed in the crystalline state is demonstrated to be both incompatible with the observed spectrum and energetically unfavorable, and it is concluded that it differs markedly from the structure in the gas phase. The potential curves for bond-length changes for the ground and excited states are discussed.

The compound [18]annulene (I) is one of a series of macrocyclic polyenes synthesized by Sondheimer[6] and is an important example of the compounds utilized

to test the generality of Hueckel's rule,[7] that $(4n + 2) \pi$ electrons will yield an aromatic system. The title compound ($n = 4$) is perhaps the most well studied of this series, but is still not fully understood. It was originally predicted that the molecule would be metastable[8] at best, by virtue of the steric crowding the inner hydrogens. Hence, its very existence as a relatively stable compound poses a challenge to our understanding of the factors affecting its stability.

(1) Paper XX: N. L. Allinger and J. C. Tai, *Theoret. Chim. Acta*, **2**, 29 (1969).
(2) This research was supported in part by Grant GP 6763, from the National Science Foundation.
(3) Abstracted in part from the Ph.D. Thesis of F. A. Van-Catledge, submitted to Wayne State University, November 1967.
(4) National Aeronautics and Space Administration Predoctoral Trainee, 1964-1967.
(5) Author to whom correspondence concerning this paper should be directed.
(6) F. Sondheimer, R. Wolovsky, and Y. Amiel, *J. Am. Chem. Soc.*, **84**, 274 (1962); and the references cited therein.
(7) E. Hueckel, *Z. Physik*, **70**, 204 (1931); **76**, 628 (1932); "Grundzuge der Theorie ungesattigter und aromatischer Verbindungen," Verlag Chemie, Berlin, 1938.
(8) K. Mislow, *J. Chem. Phys.*, **20**, 1489 (1952).
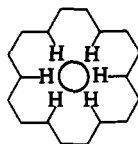
The first detailed theoretical studies on the structure of [18]annulene were carried out by Longuet-Higgins and Salem.[9] The simple MO theory of cyclic polyenes implies equal bond lengths in cyclic polyenes of the formula $C_mH_m$ ($m = 4n + 2$). This implication does not, however, include any consideration of compression of the $\sigma$ system. These authors were able to demonstrate that as $n \to \infty$ alternation *must* occur. The only question remaining was the lowest value of $n$ for which alternation could be expected. Unfortunately, this value was extremely sensitive to their choice of parameters and could be as small as 4 or as large as 8. Knowledge of this value is essential to the understanding of the annulenes. Support for the smaller value of $n$ might be sought from the fact that attempts to calculate the observed spectrum of [18]annulene with the assumption of equal bond lengths, either by perturbation techniques,[10] or by application of Moffitt's free-electron theory[11] for cyclic polyenes, failed miserably.[12]

It is well known that the pronounced diamagnetic anisotropy of simple aromatic compounds results in a deshielding of their protons, relative to simple olefins.[13] Making the simplifying assumption that this effect is due solely to the $\pi$-electronic ring currents,[14] Longuet-Higgins and Salem[9c] predicted the chemical shifts of the inner and outer protons of [18]annulene as a function of the degree of alternation. The observed nmr spectra[15] indicate that, insofar as this treatment is valid, bond alternation is occurring in [18]annulene.

The bond alternation hypothesis has fallen into disfavor on two counts. First, the structure reported for [18]annulene in the crystal state[16] shows that a type of distortion other than simple bond-length alternation is occurring. The X-ray analysis shows 12 inner bonds of mean length 1.382 ± 0.003 Å and 6 outer bonds of mean length 1.419 ± 0.004 Å, with deviations from planarity of ±0.085 Å. These authors suggest that the isolated molecule is planar.

The second piece of evidence against bond alternation is the vibronic analysis of the electronic spectrum by Gouterman and Wagniere.[17] Making use of the MO theory previously developed,[9] the potential curves for the ground and excited states of [18]annulene were calculated as a function of the degree of alternation. Suitable parameter adjustment for producing an assymmetric (bond alternation) minimum in the ground state did not displace the excited-state minimum from the symmetric (equal bond lengths) configuration. The failure to observe a vibronic progression on the $^1E_{1u}$ state in the low-temperature spectrum led these authors to conclude that bond alternation was not present. (This low-temperature study revealed the location of the $^1B_{2u}$ state, which could not be discerned in the solution spectra.) This conclusion rests upon the assumption that the effects of electronic interaction are essentially the same for all the excited states. As we shall show, this seemingly reasonable assumption has obscured the real situation.

To further confound the issue, SCFMO–CI calculations in the PPP approximation[18] based on the X-ray coordinates failed to predict the spectrum of [18]annulene satisfactorily. The calculations were carried out using a variety of integral approximations and also with inclusion of some doubly excited states. In the words of these authors, "That these extensive calculations do not predict the energy spectrum of a conjugated hydrocarbon so simple as [18]annulene is a serious failure of the SCFMO–PPP method."

In the light of this state of affairs, it seemed desirable that the problem of the electronic spectrum of [18]annulene be reinvestigated. This necessarily implies a reconsideration of the structure of this compound under normal laboratory conditions (*i.e.*, in solution or in the gas phase), for spectral properties are dependent upon the structure of the molecule, and it has not been demonstrated that the structure is invariant to phase changes.

## Method of Calculation

The basic ASMO–CI method of Pariser and Parr[19] was used as the basis for our calculation. Inasmuch as this procedure has been recently reviewed,[20,21] we will not outline it here. We will simply describe the method of evaluating the elements of the matrices $\Gamma$, $H_{CORE}$, and $C$. We have performed our calculation using the bare framework of this method, assuming no change in effective nuclear charge for carbon ($Z_C' = 3.18$) and neglecting penetration effects.[22]

**Repulsion Integrals.** The one-center repulsion integral $(CC|CC)$ was evaluated from the ionization potential and electron-affinity data for carbon given by Skinner and Pritchard.[23]

$$W_c = 11.2 \text{ eV} \tag{1}$$

$$A_c = 0.14 \text{ eV} \tag{2}$$

$$\gamma_{11} = W - A = 11.08 \text{ eV} \tag{3}$$

In evaluating the two-center repulsion integrals we have assumed that correlation effects are negligible beyond 2.41 Å and used the theoretical values calculated

(9) H. C. Longuet-Higgins and L. Salem, *Proc. Roy. Soc.* (London): (a) **A251**, 172 (1959); (b) **A255**, 435 (1960); (c) **A257**, 445 (1960).

(10) W. Davies, *Tetrahedron Letters*, No. **8**, 4 (1959).

(11) W. Moffitt, *J. Chem. Phys.*, **22**, 320 (1954).

(12) M. Gouterman and G. Wagniere, *Tetrahedron Letters*, No. **11**, 22 (1960).

(13) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp 19, 185.

(14) For a criticism of ring current theory, see J. I. Musher, *Advan. Magnetic Resonance*, **2**, 177 (1966).

(15) (a) L. M. Jackman, F. Sondheimer, Y. Amiel, D. A. Ben-Efraim, Y. Gaoni, R. Wolovsky, and A. A. Bothner-By, *J. Am. Chem. Soc.*, **84**, 4307 (1962); (b) Y. Gaoni, A. Melera, F. Sondheimer, and R. Wolovsky *Proc. Chem. Soc.*, 397 (1964).

(16) (a) J. Bergman, F. L. Hirshfeld, D. Rabinovich, and G. M. Schmidt, *Acta Cryst.* **19**, 227 (1965); (b) F. L. Hirshfeld and D. Rabinovich, *ibid.*, **19**, 235 (1965).

(17) M. Gouterman and G. Wagniere, *J. Chem. Phys.*, **36**, 1188 (1962).

(18) C. Weiss and M. Gouterman, *ibid.*, **43**, 1838 (1965).

(19) R. Pariser and R. G. Parr, *ibid.*, **21**, 466, 767 (1953).

(20) L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, Inc., New York, N. Y., 1966, pp 56 ff, 408 ff.

(21) R. G. Parr, "Quantum Theory of Molecular Electronic Structure," W. A. Benjamin, Inc., New York, N. Y., 1963.

(22) For examples of calculations including variable electronegativity and penetration effects, see N. L. Allinger, T. W. Stuart, and J. C. Tai, *J. Am. Chem. Soc.*, **90**, 2809 (1968).

(23) H. A. Skinner and H. O. Pritchard, *Trans. Faraday Soc.*, **49**, 1254 (1953).

Table I. The Calculated and Observed Spectra of Some Well-Known Conjugated Hydrocarbons

| Entry no. | Compound | Calcd eV (mμ) | f | Obsd eV (mμ) | ε | Ref |
|---|---|---|---|---|---|---|
| 1 | | 4.79 (259) | 0.0000 | 4.90 (253) | 234 | a |
| | | 5.99 (207) | 0.0000 | 6.19 (200) | 6,330 | a |
| | | 6.70 (185) | 2.2832[b] | 6.94 (179) | 120,000 | a |
| 2 | | 7.20 (172) | 0.5594 | 7.28 (170) | 17,100 | c |
| 3 | | 5.63 (220) | 0.9948 | 5.93 (209) | 25,200 | a |
| 4 | | 4.19 (296) | 0.0000 | 4.11 (302) | 270 | a |
| | | 4.85 (256) | 0.1846 | 4.53 (274) | 5,600 | a |
| | | 6.03 (206) | 2.1129 | 6.00 (207) | 120,000 | a |
| 5 | | 4.84 (256) | 0.1323 | 4.79 (259) | 3,470 | d |
| | | 5.63 (220) | 0.0000 | ε >0 at 224 mmμ Strong end abs | | d |
| | | 6.60 (188) | 0.5720 | | | |
| 6 | | 4.09 (303) | 0.0000 | 4.43 (280) | 280 | a |
| | | 5.80 (214) | 0.0000 | 6.05 (205) | Sh[e] | a |
| | | 6.45 (192) | 1.5884[b] | Strong end abs | | a |

[a] American Petroleum Institute, Project 44, Ultraviolet Absorption Data, Carnegie Institute of Technology. [b] These oscillator strengths are the sums of degenerate transitions. [c] L. C. Jones and L. W. Taylor, Anal. Chem., 27, 228 (1955). [d] W. von E. Doering and L. H. Knox, J. Am. Chem. Soc., 79, 352 (1957). [e] Sh = shoulder.

according to Roothaan's formulations.[24] At distances <2.41 Å we have employed a previously derived[25] parabolic function for planar systems (eq 4). For nonparallel

$$\gamma_{ab}{}^{emp}(eV) = 11.08 - 3.92327 r_{ab} + 0.69786 r_{ab}{}^2 \quad (4)$$

orbitals we have employed the relationship[26]

$$\gamma_{ab}{}^{emp} = \gamma_{\pi\pi}{}^{emp}(\gamma_{ab}{}^{theo}/\gamma_{\pi\pi}{}^{theo}) \quad (5)$$

**Elements of $H_{CORE}$.** The diagonal elements of $H_{CORE}$ were evaluated in the customary manner,[19] neglecting penetration.

$$\mathbf{H}_{pp} = -W_c - \sum_{q \neq p}(pp|qq) \quad (6)$$

Off-diagonal elements were defined as

$$\mathbf{H}_{pq} \equiv \beta_{pq} = 0 \quad (7)$$

unless $p$ and $q$ are neighbors. For neighboring atoms, $\beta$ was defined as

$$\beta_{pq} = (\cos\alpha_p \cos\alpha_q)\beta_{pq}{}^\sigma + (\sin\alpha_p \sin\alpha_q) \cos\omega\beta_{pq}{}^\pi \quad (8)$$

where $\alpha_p$ is the angle formed by the positive end of the axis of the $\pi$ orbital on atom $p$ with the internuclear axis and $\omega$ is the dihedral angle defined by the two $\pi$ orbitals.

(24) C. C. J. Roothaan, J. Chem. Phys., 19, 1445 (1951); 22, 765 (1954).
(25) N. L. Allinger and M. A. Miller, J. Am. Chem. Soc., 86, 2811 (1964).
(26) This technique has been found to give more reasonable transition energies: M. A. Miller, unpublished results.

The required $\beta$'s were evaluated at $r_{pq}$ from Mulliken's formula[27] as

$$\beta_{pq}{}^{\pi,\sigma} = -11.7040 A^{\pi,\sigma}(S_{pq}{}^{\pi,\sigma}/(1 + S_{pq}{}^{\pi,\sigma})) \text{ eV} \quad (9)$$

where $A^{\pi,\sigma}$ is a symmetry constant ($A^\pi = 1.0$, $A^\sigma = 0.773$) and $S_{pq}{}^{\pi,\sigma}$ is the appropriate overlap integral evaluated through Roothaan's equations.[24]

**Orbital Coefficients.** We were interested in using the best possible MO's in the LCAO approximation,

$$\phi_i = \sum_p C_{ip}\chi_p \quad (10)$$

and therefore proceeded to solve the Hartree-Fock-Roothaan equations[28] in ZDO approximation. It has been shown[29-31] that when configuration interaction is limited to singly excited states, the accuracy of the final predicted transition energies is clearly enhanced by the use of SCF orbitals. We have also incorporated into our iterative SCF program a procedure for producing the symmetry orbitals from the F matrix. The technique used is essentially that described by Streitwieser.[32] Self-consistency was considered to have been reached when

(27) R. S. Mulliken, J. Am. Chem. Soc., 72, 4493 (1950); J. Phys. Chem., 56, 295 (1952).
(28) C. C. J. Roothaan, Rev. Mod. Phys., 23, 69 (1951).
(29) N. L. Allinger and J. C. Tai, J. Am. Chem. Soc., 87, 2081 (1965).
(30) N. L. Allinger and T. W. Stuart, J. Chem. Phys., 47, 4611 (1967).
(31) Our pilot studies showed that this improvement results primarily from changes in the excited-state energies rather than that of the ground state.
(32) A. Streitwieser "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, N. Y., 1961, Chapter 3.

**Table II.** The Calculated Spectra for Various Models of [18]Annulene

| Excited state | Obsd[a,b] eV (mμ) | ε | I-XP eV (mμ) | f | I-XNP eV (mμ) | f | I-EP eV (mμ) | f | I-AP eV (mμ) | f | I-ANP eV (mμ) | f |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $^1B_{2u}$ | 2.52 (491) | ~100[c] | 1.36 (913) | 0.0000 | 1.17 (1053) | 0.0000 | 1.34 (923) | 0.0000 | 3.61 (343) | 0.0000 | 5.37 (231) | 0.0000 |
| $^1B_{1u}$ | 2.65 (468) | ~20,000[d] | 1.96 (633) | 0.0000 | 1.83 (677) | 0.0000 | 1.93 (641) | 0.0000 | 2.74 (453) | 0.0000 | 4.13 (300) | 0.0183 |
| $^1E_{1u}$ | 4.03 (308) | ~300,000 | 4.26 (291) | 8.5124[e] | 4.07 (305) | 8.4700[e] | 4.24 (293) | 8.3852[e] | 4.23 (293) | 4.2434[e] | 5.02 (247) | 1.4238[f] |
|  |  |  |  |  |  |  |  |  |  |  | 5.03 (247) | 1.4092[f] |

[a] Taken from ref 18. [b] These transition energies have been corrected to the gas phase. [c] This is our estimate of the extinction coefficient for this transition. [d] This extinction coefficient is for the second member in the $^1B_{1u}$ progression. [e] These oscillator strengths represent the sums for both $^1E_{1u}$ transitions. [f] The loss of degeneracy here is due to slight deviations from $D_3$ symmetry in our starting coordinates.

the change in all coefficients was less than $10^{-7}$ from one iteration to the next. The calculations were carried out using double-precision arithmetic.

**Configuration Interaction.** The computational procedure for carrying out the CI calculation and calculation of transition energies and oscillator strengths has been previously described.[25]

All calculations were carried on an IBM 7074 computer. The sequence of programs had to be segmented to overcome storage limitations. Due to the use of double precision arithmetic, the running times were quite long (~50 min) for naphthalene, 5-6 hr for an [18]annulene).

**Numerical Results**

**Preliminary Calculations.** Before proceeding to a consideration of [18]annulene itself, we felt it desirable to test the accuracy of our computational scheme by calculating the transition energies of some well-known hydrocarbons. For accurate comparison we have corrected the experimentally observed transitions to the gas phase by the method of Bayliss.[33] It should be borne in mind that our calculated transition energies are Franck-Condon bands for the equilibrium geometry of the ground states of these molecules.

Most calculations of this nature begin with benzene. Assuming a regular hexagon with sides 1.397 Å in length,[34] we are able to predict the experimental transitions to within 0.25 eV. An error of this magnitude is relatively insignificant, in terms of wavelength, in the region of 7.0 eV, but can be quite discomforting at lower energies (see entry 4, Table I). Our oscillator strength values are generally too large by a factor of 2 or 3, but the relative transition probabilities of the three transitions are well accounted for. It will be recalled that the observed intensities of the $^1B_{1u}$ and $^1B_{2u}$ states have been shown to arise from vibrational interaction of these with the allowed $^1E_{1u}$ states.[11,35] This data is entry 1 in Table I.

For ethylene (entry 2), we have assumed a bond length of 1.334 Å, and for all practical purposes, duplicated the experimentally observed maximum. The goodness of

fit is marred, however, by the ambiguities imposed by the vibronic structure of the peak in question.[36]

Turning now to the allowed transition for *trans*-butadiene (entry 3), we find that our calculated transition is 0.3 eV too small, using the recently determined geometry for this molecule.[37] We feel that this is a manifestation of a systematic error in our calculations. Comment on this will be reserved until the end of this section.

The last of our planar systems, naphthalene (entry 4), has been reported to have two slightly different geometries in the literature.[38,39] To facilitate comparison with other work from this laboratory,[40] we have used the Cruickshank[38] parameters. Our calculated values for the first and third transitions are very good. The calculated second transition is markedly higher than the observed value. This may be the result of the geometry chosen, or it may be indicative of the desirability of including multiply excited states in the CI calculations.[30]

Tropilidene (entry 5) has been shown, both theoretically[41] and experimentally,[42] to exist in a boat-like conformation. Our calculated transitions are in excellent agreement with the experimental values,[43] and also with the previously predicted values.[41]

With cyclooctatetraene (entry 6), using the Traetteberg geometry,[37] we note again the trend towards low values for calculated transition energies. The disagreement in the first transition (0.34 eV) is probably not so serious as it seems, as this peak is observed experimentally as a rather broad band whose maximum is not accurately discernible, and the general features of the spectrum are well accounted for. (It is also possible that the observed transition is $\pi \rightarrow \sigma^*$.)

There are two features of these preliminary results to be noted. First, despite one or two large discrepancies, our over-all standard deviation is ±0.21 eV, which compares favorably with the current level of experimental

(33) N. S. Bayliss, *J. Chem. Phys.*, **8**, 292 (1950).
(34) (a) A. Almenningen, O. Bastiansen, and L. Fernholt, *Kgl. Norske Videnskab. Selskabs Skrifter*, No. 3, 1 (1958); (b) A. Langseth and B. P. Stoicheff, *Can. J. Phys.*, **34**, 350 (1956).
(35) M. Goeppert-Mayer and A. Sklar, *J. Chem. Phys.* **6**, 645 (1938).
(36) L. C. Jones and L. W. Taylor, *Anal. Chem.*, **27**, 228 (1955).
(37) M. Traetteberg, *Acta Chem. Scand.*, **20**, 1724, 1726 (1966).
(38) D. W. J. Cruickshank and R. A. Sparks, *Proc. Roy. Soc.* (London), **A258**, 270 (1960).
(39) A. Almenningen, O. Bastiansen, and F. Dyrik, *Acta Cryst.*, **14**, 1056 (1961).
(40) N. L. Allinger, J. C. Tai, and T. W. Stuart, *Theo. Chim. Acta*, **8**, 101 (1967).
(41) N. L. Allinger, M. A. Miller, L. W. Chow, R. A. Ford, and J. C. Graham, *J. Am. Chem. Soc.*, **87**, 3430 (1965).
(42) M. Traetteberg, *ibid.*, **86**, 4265 (1964).
(43) W. von E. Doering and L. H. Knox, *ibid.*, **79**, 352 (1957).

Table III. The Approximate Total Energies for the Various Forms Considered for [18]Annulene[a]

| Energy component | | I-XP | I-XNP | Structure I-EP | I-AP | I-ANP |
|---|---|---|---|---|---|---|
| $E_\pi$[b] | | −5446.3 | −5329.2 | −5432.2 | −5467.2 | −5382.5 |
| $E_\sigma$ | | 110.9 | 110.9 | 93.4 | 124.3 | 124.3 |
| $E_{VDW}$ | | 83.2 (48.5)[c] | −0.3 (−0.2)[c] | 82.1 (47.8)[c] | 79.7 (46.4)[c] | 0.4 (0.5)[c] |
| $E_{total}$ | | −5252.2 (−5286.9)[c] | −5218.6 (−5218.5)[c] | −5256.7 (−5291.0)[c] | −5263.2 (−5296.5)[c] | −5257.8 (−5257.8)[c] |
| $E_{rel}$[d] | I | 4.5 (4.1)[c] | 38.1 (72.5)[c] | 0.0 (0.0)[c] | −6.5 (−5.5)[c] | −1.1 (31.3)[c] |
| | II | | | | | |

[a] All energies are in kilocalories/mole. [b] Taken from our SCF calculations. [c] The parenthesized numbers are calculated using the van der Waals' parameters of set II. [d] $E_{rel}$ is referred to $E_{total} = 0$ for I-EP.

accuracy (0.20 eV). Second, we noted that those bond lengths which did not involve nonparallel p orbitals could be accommodated by the SCF bond order–bond length relationship (eq 11). The only exception to this

$$r_{ij} = (1.523 - 0.189 p_{ij}) \text{ Å} \qquad (11)$$

is the 1,2 bond in naphthalene which is implied to be 0.01 Å too short. The other bond lengths are predicted to within 0.004 Å. It should be noted that the other geometry reported[39] for naphthalene does show a longer 1,2 bond. Further investigation is required to determine whether or not this difference is significant.

No attempt was made to optimize parameters, since small changes would have little or no effect on the structural features with which we are here concerned. The better parameter set used earlier[41] could not be employed here as it requires configuration interaction of all doubly excited configurations, an operation quite beyond our available computer facilities in the case of [18]annulene.

Before describing our results for [18]annulene, we should like to comment on the assignments of excited states made in Table II. (The symmetry designations used are formally correct only for the first and third models, but we have retained them for simplicity's sake.) The transitions of interest arise primarily from excitations from $\phi_8$ and $\phi_9$ to $\phi_{10}$ and $\phi_{11}$. (In [18]annulene, in contrast to benzene, there are many singly excited states of higher energy that mix slightly into the low energy transitions; but these low-lying states retain 80–95% four-orbital character.) It is well known that in alternate hydrocarbons these four orbitals are related as[44]

Highest Occupied MO's

$$\phi_i = \sum {}^* a_i \chi_i + \sum {}^0 a_j \chi_j \qquad (12)$$

$$\phi_j = \sum {}^* b_i \chi_i + \sum {}^0 b_j \chi_j \qquad (13)$$

Lowest Unoccupied MO's

$$\phi_k = \sum {}^* a_i \chi_i - \sum {}^0 a_j \chi_j \qquad (14)$$

$$\phi_l = \sum {}^* b_i \chi_i - \sum {}^0 b_j \chi_j \qquad (15)$$

where the summations $\sum {}^*$ and $\sum {}^0$ are over "starred" and "unstarred" atoms, respectively. We have taken the $^1B_{2u}$ states as arising from forbidden transitions between "unpaired" MO's, e.g., $\phi_{i \to l}$, and the $^1B_{1u}$ states

(44) (a) M. J. S. Dewar and H. C. Longuet-Higgins, Proc. Phys. Soc., A67, 795 (1954); (b) J. A. Pople, ibid., A68, 81 (1955).
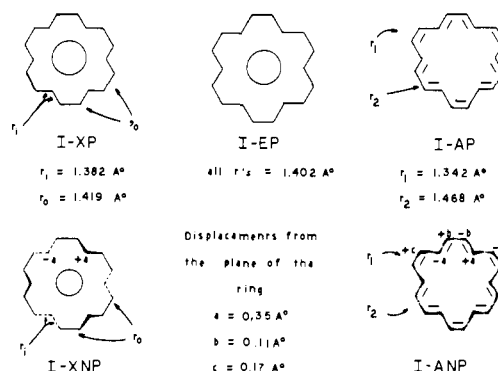
Figure 1. Representations of the models used for [18]annulene.

I-XP r₁ = 1.382 A° r₀ = 1.419 A°
I-EP all r's = 1.402 A°
I-AP r₁ = 1.342 A° r₂ = 1.468 A°
I-XNP
Displacements from the plane of the ring: a = 0.35 A°, b = 0.11 A°, c = 0.17 A°
I-ANP

as arising from forbidden transitions between "paired" MO's, e.g., $\phi_{i \to k}$. For our experimental transition energies we have taken the assignments made by Gouterman and Wagniere,[17] since this is the most detailed analysis of the spectrum. The first peaks in the $^1B_{2u}$ and $^1B_{1u}$ progressions are essentially unaffected by our solvent correction, but the correction on the $^1E_{1u}$ state amounts to some 0.70 eV ($\sim 65$ mμ), insofar as our equation is valid. The best argument in support of this value is the constancy of the predicted $^1E_{1u}$ transition energy among most of the models considered, which coincides almost exactly with the corrected value.

We have considered five models (see Figure 1) for [18] annulene. Structure I-XP was assigned the mean X-ray bond lengths and 120° C–C–C angles. These angles were used for convenience sake. If the calculations had shown promise, we would have adjusted this structure to more nearly approximate the one observed in the crystal. The calculated $^1E_{1u}$ transition energy compares favorably with our projected vapor phase value, but the $^1B_{2u}$ and $^1B_{1u}$ states are much too far to the red (Table II). The error in these cases is on the order of 1.0 eV, which we feel is too large to ascribe to errors in the calculation, and we conclude that the molecule does not have this structure in solution.

Structure I-XNP preserved the X-ray bond lengths but had the inner carbons displaced 0.35 Å from the plane of the ring. This is the amount of carbon puckering implied by Coulson and Golebiewski[45] in their calculations on the strain energy of [18]annulene. The "corre-
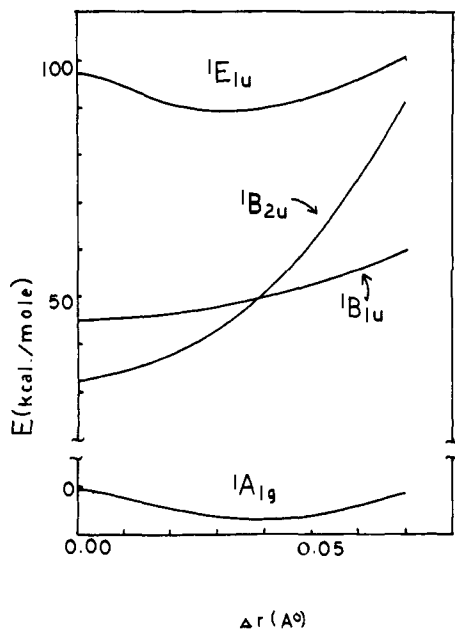
Figure 2. Approximate potential energy curves for the ground and excited states of [18]annulene as a function of the alternation parameter $\Delta r$ ($r_1 = 1.405 - \Delta r$; $r_2 = 1.405 + \Delta r$). The zero of energy is the ground state of the symmetric configuration ($\Delta r = 0$).

gated" conformation was demonstrated by them to be the most favorable type of deformation. In this structure we have assumed no formal double bonds and maintained the outer carbons in a plane. The net result is a system of six coupled allylic units. There have been contradictory predictions as to the effect of this type of deformation on the transition energies. Coulson[45] has suggested a lowering of the transition energies while Woodward[46] has suggested the opposite effect. Our calculations show that the former suggestion is probably the correct one, as all of the transitions are displaced to lower energy with no improvement in the spectral fit.

The SCF bond orders for I-XP ($P_{inner} = 0.639$; $P_{outer} = 0.641$) implied, through eq 11, a structure having equal bond lengths of 1.402 Å. This structure (I-EP) was subjected to our calculations and proved to be virtually indistinguishable from I-XP, as far as the calculated spectrum was concerned.

All of the results we have described thus far confirm the findings of others,[10,12,18] that neither the X-ray structure nor one having equal bond lengths can be reconciled with the observed spectrum. If the PPP method were untested, we would be inclined to question its applicability to the system at hand. Since, however, this method has enjoyed a good deal of success over a wide range of compounds, we must question the veracity of the models we have used to this point. We have, in this light, generated a markedly alternated planar structure, I-AP, and calculated its theoretical spectrum. The changes manifested are quite drastic. The transition energy of the $^1E_{1u}$ state is essentially unchanged, but the oscillator strength has been reduced to $\sim 50\%$ of its value in I-XP, etc. The $^1B_{1u}$ state has a somewhat higher energy (41%), while that of the $^1B_{2u}$ state has increased by 167%, which lowers

the predicted wavelength from 913 m$\mu$ in the regular model to only 343 m$\mu$ in the alternating one.

As another model, we have considered the effect of nonplanarity on I-AP by puckering it to give I-ANP. In this model the formal double bonds were preserved, along with the 120° bond angles. The displacement of the inner carbons was the same as for I-XNP. This type of "corrugation" resulted in a structure of $D_3$ symmetry having no carbon in the mean plane of the ring. The coordinates for this geometry were difficult to derive, and small deviations from $D_3$ symmetry are responsible for the loss of degeneracy in the $^1E_{1u}$ states and the nonzero oscillator strength of the $^1B_{1u}$ state. All states have increased in energy and the ubiquitous $^1B_{2u}$ state is now the state of highest energy.

## Discussion

**Ground-State Energies.** The structure I-AP yields the kind of "compressed" spectrum observed for [18]annulene. This would cause one to suspect that bond alternation is the key to understanding this spectrum, though not to so great a degree as we have assumed. We may next consider the relative total energies among the various forms. In order to do this, we require a function for the $\sigma$ compression energy. We have derived a Hooke's law type of function from the relationship

$$\sum_i [(\partial E_\pi/\partial r_i) + (\partial E_\sigma/\partial r_i)] = 0 \qquad (16)$$

where $i$ is over all carbon–carbon bonds. From the quantities $\partial E_\pi/\partial r_i$ for benzene and ethylene at their respective equilibrium distances, we obtained the function (see Appendix)

$$E_\sigma = 508.6(r - 1.503 \text{ Å})^2 \text{ kcal/mol} \qquad (17)$$

This potential function includes, in an average manner, penetration effects and the van der Waals interaction among the atoms bound to the carbons of the double bond. The other van der Waals interactions can be assumed to be essentially constant for the molecules we are considering. In [18]annulene however, we must also consider the interactions among the internal hydrogens. In order to do this, we have used the Hill equation[47]

$$E_{ij} = \varepsilon_{ij}\{(-2.25/B^6) + 8.28 \times 10^5 \exp(9 - [B/0.0736])\} \qquad (18)$$

$$B = D_{ij}/(R_i^* + R_j^*)$$

$$\varepsilon_{ij} = (\varepsilon_i \varepsilon_j)^{1/2}$$

where $D_{ij}$ is the distance in ångströms between atoms $i$ and $j$, $R_i^*$ is the van der Waals radius of atom $i$, and $\varepsilon$ is the energy parameter for atom $i$ in kilocalories/mole. We have used two sets of parameters. Set I is taken from some work on the calculation of conformational energies ($R_H^* = 1.50$ Å, $\varepsilon_H = 0.049$ kcal/mol.[48] Set II was inspired by similar studies[49] which assumed that the van der Waals center is located $0.872R_{C-H}$ Å away from the carbon, rather than at the hydrogen nucleus. We believe the following is the best set of parameters available to

(45) C. A. Coulson and A. Golebiewski, *Tetrahedron*, **11**, 125 (1960).
(46) Cited in ref 20, p 509.

(47) T. L. Hill, *J. Chem. Phys.*, **16**, 399 (1948).
(48) N. L. Allinger, M. A. Miller, F. A. Van-Catledge, and J. A. Hirsch, *J. Am. Chem. Soc.*, **89**, 4345 (1967).
(49) D. E. Williams, *J. Chem. Phys.*, **45**, 3770 (1966).

date for use with the Hill equation: $R_H{}^* = 1.50$ Å, $\varepsilon_H = 0.056$ kcal/mol.[50] The results of these calculations are summarized in Table III.

The nonplanar form I-XNP is seen to be unreasonably strained in either van der Waals approximation and may be dismissed from further consideration. For I-ANP, the destabilization may be as small as 5.4 kcal/mol (VDW Set I) or as large as 36.8 kcal/mol (VDW Set II), relative to I-AP. Our inclination in this matter is toward the results obtained with set II, as this type of model for hydrogen has proved most successful in accounting for the crystal structure of aromatic hydrocarbons[49] and is closely related to the model successfully employed by Lowe and Parr[51] in their theoretical studies of rotational barriers. The molecule therefore must be very close to planar.

Confining our attention to the planar structures, we find that the relative energies among the planar forms are essentially independent of the van der Waals parameters used. This fact gives us a good deal of confidence in the qualitative aspects of our results. The X-ray structure (I-XP) can be seen to be slightly higher in energy than the one having equal bond lengths (I-EP). We are convinced that this difference is real, and would like to suggest that the observed crystal structure may be caused by the lack of trigonal symmetry which arises in the following manner. The effects of this type of distortion on bonding have been discussed by Murrell and Hirchliffe.[52] Compression of [18]annulene into the crystal restricts the out-of-plane C–H deformations thereby increasing the van der Waals energy. This, in turn, causes compression of the inner C–H and C–C bonds, with the outer C–C bonds adjusting in such a manner as to minimize the total energy. Lattice forces within the crystal have not yet been well accounted for.[16b]

The alternating structure I-AP is calculated to be the favored configuration by 5 kcal/mol. We should like to point out that while I-EP represents to within 0.003 Å the symmetric configuration of minimum energy,[10,17] the alternating structure I-AP probably does not represent the asymmetric configuration of lowest energy. This is implied through eq 11, which suggests that the degree of alternation $(r_2 - r_1 = 0.126$ Å$)$ is too large. The important fact to be gleaned from this is that [18]annulene has a potential curve with a shallow minimum with respect to bond alternation. This type of potential curve has been predicted in other cases.[53,54]

The results just described have been checked by using an incorrect $\sigma$ compression function (for our calculations) taken from work that included penetration effects in the $\pi$ calculations.[55] The magnitude of the energy differences change, but the qualitative relationships among the various forms does not. Finally, we have derived a Morse function (see Appendix) which is more appropriate for this kind of calculation (eq 19)

$$E_c = D\{1 - \exp[-a(r - r_0)]\}^2 \qquad (19)$$

where $D = 896.6$ kcal/mol, $a = 0.6495$ Å$^{-1}$, and $r_0 = 1.523$ Å (from eq 11). The relative energies for I-XP and I-AP are $+4.3$ $(+3.9)$ and $-9.0$ $(-8.0)$ kcal/mol, respectively, with the parenthesized values corresponding to set II of our van der Waals parameters. Inasmuch as the energetic relationship I-XP > I-EP > I-AP is invariant under the various permutations of potential energy functions, we are reasonably sure that it is the correct one.

**Potential Energy Curves.** We believe the discussion given above establishes a theoretical basis for the structure of the ground state configuration of the isolated [18]-annulene molecule. Before one can fully understand the spectrum, however, the nature of the potential curves for the excited states must be likewise elucidated. From the changes in the various state energies in going from I-EP to I-AP we have drawn the following conclusions. For the $^1E_{1u}$ state, whose transition energy is essentially constant, we suggest a potential curve which closely parallels that of the ground state, i.e., a minimum in the asymmetric configuration. For the $^1B_{1u}$ state, the transition energy has increased somewhat, implying a rather broad potential curve having its minimum at the symmetric configuration. Finally, the transition energy for the $^1B_{2u}$ state has risen sharply, thereby implying a rather narrow potential curve, having its minimum, again, at the symmetric configuration. A qualitative representation of these curves is given in Figure 2.

Two points are in fact inadequate for defining any curve other than a straight line, hence it would have been desirable to do full treatments on two or three geometries intermediate between I-EP and I-AP. The exceedingly long running times for these structures were prohibitive in this regard. Some more approximate results (varying $\Delta r$ over the range 0.0–0.07 Å) using only first-order CI after the method of Pople,[45b] show a ground-state minimum in the region $r_1 = 1.365$ Å, $r_2 = 1.445$ Å. This is the only asymmetric configuration at which the SCF bond orders imply the bond lengths used. These calculations also confirm that the conclusions regarding the shapes of the potential curves for the excited states are indeed correct. We can see now that the previous predictions[17] based on excited-state curves without consideration of electronic interaction were quite misleading, for each of the excited states behaves in an independent manner.

To round out the picture, we have calculated the spectrum of a bond-alternated model for [18]annulene having the bond lengths given by our energy calculation. These results are shown in Table IV. Neither the largest difference (0.37 eV for the $^1B_{1u}$ state) nor the standard deviation (0.25 eV) differs significantly from that obtained with our test compounds (Table I). We feel therefore that this constitutes a good spectral fit within the limits of accuracy of our parameterization,[56] and we suggest that this structure is a much better approximation to the structure of the isolated molecule than that found by X-ray crystallography.

The observed low-temperature spectrum[17] can now be

(50) J. T. Sprague, unpublished results.

(51) J. P. Lowe and R. G. Parr, *J. Chem. Phys.*, **43**, 2565 (1965), and references cited therein.

(52) J. N. Murrell and A. Hirchliffe, *Trans. Faraday Soc.*, **62**, 2011 (1966).

(53) M. Tsuji, S. Huzinaga, and T. Hasino, *Rev. Mod. Phys.*, **32**, 425 (1960).

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

(55) N. L. Allinger, C. Gilardeau, and L. W. Chow, *Tetrahedron*, **24**, 2401 (1968).

(56) In principle there should be four bond lengths for the alternated species, the inner bonds being different from the outer ones. Our bond order calculations show this to be true, but the differences are very small. For the short bond, $r_{inner} = 1.364$ and $r_{outer} = 1.362$ Å, while for the long bond $r_{inner} = 1.448$ and $_{outer} = 1.444$ Å.

Table IV. The Calculated Spectrum for the Proposed Equilibrium Structure of [18]Annulene[a,b]

| Excited state | Obsd eV (mμ) | ε | Calcd eV (mμ) | f |
|---|---|---|---|---|
| $^1B_{2u}$ | 2.52 (491) | 100 | 2.42 (513) | 0.000 |
| $^1B_{1u}$ | 2.65 (468) | 20,000 | 3.02 (410) | 0.000 |
| $^1E_{1u}$ | 4.03 (308) | 300,000 | 4.08 (304) | 4.840 |

[a] $r_1 = 1.365$ Å, $r_2 = 1.445$ Å.  [b] See footnotes a–d, Table II.

readily interpreted. The $^1E_{1u}$ transition should have its intensity concentrated in the 0–0 band with negligible intensity in the high members. The $^1B_{1u}$ transition should have an 0–0, 0–2, 0–4, type of progression, with intensity concentrated in the second member in the series. Lastly, the $^1B_{2u}$ transition should show a weak 0–$n$ progression for all values of $n$. This is precisely the type of spectrum observed.

## Conclusions

We conclude that the [18]annulene molecules in solution or in the gas phase exist in a bond-alternated configuration, as originally proposed[9] with $\Delta r \approx 0.08$ Å. This interpretation permits explanation of the observed uv and nmr spectra. The only reason for questioning this has been the observed structure in the crystal state. We feel that this is the sole anomaly in the reported observables, and have suggested why this might be the case. We feel that deviations from planarity among the carbons are small at room temperature, but that the out-of-plane C–H deformations may be fairly large. As the barrier between the two equivalent configurations is fairly small (perhaps 10 kcal/mol), we should like to revive the suggestion that dynamic alternation[17] is occurring at room temperature. This idea is supported by the lack of resolution of the two peaks in the nmr spectrum at room temperature.[15] Increasing the temperature should cause the out-of-plane deformations of all the atoms to become sufficiently large so as to permit the hydrogens to exchange positions, thereby giving the single line spectrum observed. Deformations of the type depicted for I-ANP will permit this phenomenon to occur as a wave, moving around the ring, without extensive loss of conjugation. We calculate $\Delta G^*$ for this process (from the reported nmr data) as 16 kcal/mol. Finally, regarding Hueckel's rule of $(4n + 2)$ $\pi$ electrons for enhanced stability (aromaticity), the experimental stabilization energy for [18]annulene is 100 kcal/mol,[57] which we feel requires no comment.

Inasmuch as alternation has set in with [18]annulene, we feel it safe to assume that the higher annulenes should rapidly approach the degree of alternation observed in butadiene $(r_{23} - r_{12} = 0.126$ Å). It may well be that benzene is the only physically real annulene which is definitely more stable in the symmetric configuration.

(57) A. E. Beezer, C. T. Mortimer, H. D. Springall, F. Sonheimer, and R. Wolovsky, J. Chem. Soc., 216 (1965).

## Appendix

One of our referees has requested that the derivations of our $\sigma$ compression functions (eq 17 and 19) be given. The equilibrium structure of a compound is taken to be that configuration whose total energy is at a minimum with respect to each bond $r_i$, i.e.

$$\sum_i (dE_{total}/dr_i) = \sum_i [\partial E_\pi/\partial r_i) + (\partial E_\sigma/\partial r_i)] = 0 \quad (A1)$$

We have calculated the $\pi$ energy for ethylene as a function of internuclear distance and, by taking sufficiently small increments (0.001 Å), obtained the slope $(S_e)$ for this quantity at the equilibrium bond length. Similarly, we have calculated the $\pi$ energy for benzene as a function of bond length, maintaining $D_{6h}$ symmetry, and obtained its slope $(S_b)$ at the equilibrium distance. The slopes thus obtained were used in the relationship

$$(S_b/S_e) = 6[f'(r_b)/f'(r_e)] \quad (A2)$$

where $f(r)$ may be either a parabolic function or a Morse function. (The factor of 6 arises because of the six bonds in benzene.) In the case of the parabolic function (eq 16), both $k$ and $r_0$ are readily deduced by the appropriate algebraic manipulations. For the Morse function (eq 19), however, things are not so straightforward. One must assume a value for $a$ and solve for $r_0$ by successive approximations, or conversely, assume $r_0$ and solve for $a$. We have no way of deciding upon a reasonable value for $a$, so we have taken $r_0$ as the zero bond order–bond length of eq 11. The rationale for this is that $r_0$ represents the "natural" $C_{sp^2}$–$C_{sp^2}$ single bond length in the absence of $\pi$ bonding. While this value is slightly larger than those generally accepted[58] (based, in part, on the $C_{sp^3}$–$C_{sp^2}$ single bond length in propene of 1.501 Å[59]), we feel this to be a realistic estimate. It has been demonstrated that the assumption of no $\pi$ bonding across the formally single bonds in ethane, propene, and propyne is not a valid one.[60,61]

(58) Reference 20, p 134f.

(59) D. R. Lide, Tetrahedron, 17, 125 (1962).

(60) M. D. Newton and W. N. Lipscomb, J. Am. Chem. Soc., 89, 4261 (1967), and references cited therein.

(61) NOTE ADDED IN PROOF. Subsequent to the submission of this manuscript, a long-wavelength band at ∼13,000 cm⁻¹ (1.6 eV) was reported in the spectrum of [18]annulene [H.-R. Blattmann, E. Heilbronner, and G. Wagnière, J. Am. Chem. Soc., 90, 4786 (1968). We have corresponded with these authors, informing them of our results, and they have been kind enough to appraise us of their more recent work, which they are preparing for publication. We should like to make two suggestions at this time. First, the assignment made by Gouterman, et al. (see ref 17) for the ¹B₂ᵤ state is correct, based on the calculations described in this paper. Second, the long-wavelength band observed by Heilbronner and coworkers in the spectrum of [18]annulene probably corresponds to an electronically allowed π ↔ σ transition [see M. Robin, H. Basch, N. A. Kuebler, B. E. Kaplan, and J. Meinwald, J. Chem. Phys., 48, 5037 (1968), and the references cited therein], whose intensity and fine structure would be dependent upon the extent of out-of-plane deformation. The details and intensity of this band should, therefore, be quite temperature dependent, as is the nmr spectrum of [18]annulene. These suggestions are quite in line with the results which Professor Heilbronner has generously communicated to us.