ORGANIC AND BIOLOGICAL CHEMISTRY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WAYNE STATE UNIVERSITY, DETROIT 2, MICHIGAN]

Organic Quantum Chemistry. VII. Calculation of the Near-Ultraviolet Spectra of Polyolefins[1,2]

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The π-electronic spectra have been calculated for a number of dienes and trienes, conjugated, unconjugated, and cross-conjugated, utilizing the basic method of Pariser and Parr but with modification of the numerical values of certain of the required integrals. Butadiene was studied as the s-cis and s-trans conformers, and for various rotational arrangements intermediate between these extremes. It was usually found possible to calculate the wave lengths of the observable transitions to within 5–10 mμ, and to obtain reasonable estimates of the oscillator strengths.

Introduction

The ultraviolet spectra of organic compounds have been of considerable use to organic chemists from the point of view of structural determination.[4] There are available empirical rules by which the spectrum of a compound which belongs to one of certain selected classes can be predicted with a high degree of accuracy. Woodward's rules[5] offer a very practical method for the prediction of the absorption maximum in the ultraviolet spectrum of a conjugated polyene, as long as it belongs to a rather select, almost planar, noncross-conjugated system containing bond angles close to normal. There are any number of interesting compounds available which do not possess all of the appropriate characteristics, and for which the simple rules are inapplicable. We have therefore considered the very practical problem of the prediction of the spectra of olefins in general: conjugated, unconjugated, or cross-conjugated, and possessing any number of double bonds in any spatial orientation. There is available a theoretical method for the calculation of such spectra, which was developed by Pariser and Parr,[6,7] and which was applied by them to a few simple systems. The quantum mechanical calculation of the electronic properties of even a simple polyene would be prohibitively laborious unless various approximations were made. The Pariser–Parr method, which has been relatively accurate in the limited area to which it has been applied, makes two kinds of approximations. One is the wholesale neglect of large numbers of integrals which enter into the calculation on the basis that they are quite small. The second approximation, which in part compensates for errors introduced by the first, is to use empirical rather than theoretical values for certain specified integrals.

The Pariser–Parr method has not been extensively applied to polyenes previously,[7–10] and there is considerable uncertainty as to what kind of accuracy is to be

(1) Paper VI: N. L. Allinger, L. A. Frieberg, R. B. Hermann, and M. A. Miller, J. Am. Chem. Soc., 85, 1171 (1963).

(2) This research was supported in part by Grants G-10346 and G-19981 from the National Science Foundation.

(3) Predoctoral National Institutes of Health Fellow, Division of General Medical Sciences, 1962–1963.

(4) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962.

(5) L. F. Fieser and M. Fieser, "Steroids." Reinhold Publishing Corp., New York, N. Y., 1959, p. 16.

(6) R. Pariser and R. G. Parr, J. Chem. Phys., 21, 466, 767 (1953).

(7) R. Pariser, ibid., 24, 250 (1956).

(8) P. Schiess and A. Pullman, J. chim. phys., 53, 101 (1956).

(9) C. F. Wilcox, Jr., S. Winstein, and W. G. McMillan, J. Am. Chem. Soc., 82, 5450 (1960).

(10) R. B. Hermann, J. Org. Chem., 27, 441 (1962).

expected from the calculations. We have therefore selected a number of examples of olefins for which experimental data are available for comparison, and which contain all of the different kinds of features in which one is interested. In this paper we will discuss only the olefinic portion of the system; the effect of substituents such as methyl groups or alkoxyl groups will be deferred to a later paper. The compounds for which calculations have actually been made in the present work are butadiene (II) (as a function of the rotational angle about the C–C single bond), 1,3,5-hexatriene (III) (in all of its planar conformations), bicycloheptadiene (or norbornadiene) (IV), bicyclo[2.2.2]-2,5,7-octatriene (V), tetrahydroacepentylene (VII), and sym-cis,cis,cis-1,4,7-cyclononatriene (VI).
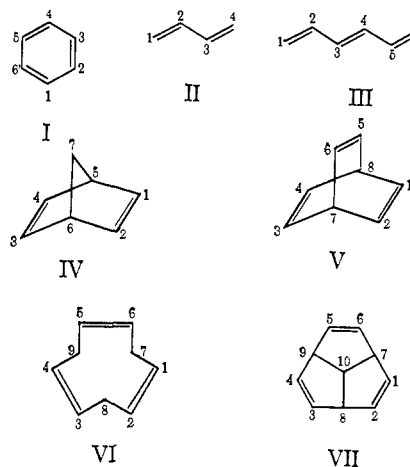
Mathematical Method

The π-electron approximation is used throughout the present work, including for the nonplanar systems in which its validity is much less certain than for the planar systems. This approximation is necessary at this time if the problems are to be held to manageable size, and its validity will ultimately be found in the agreement between experimental and calculated quantities. Only the π-electrons are treated explicitly; the σ-electrons together with the nuclei form the "core" or the field in which the π-electrons move. Thus, for a molecule with n π-electrons, moving in the field of the core, the π-electron Hamiltonian operator is written

$$\mathcal{3C} = \sum_{i=1}^{n} \mathbf{H}_{core}(i) + \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} (e^2/r_{ij}) \qquad (1)$$

The n-electron system wave functions are built from normalized antisymmetrized product functions, expressed as Slater determinants. The molecular orbitals (MO) are taken to be ortho-

normal combinations of the atomic orbitals (AO) involved in the system being treated.

$$\phi_i = \sum_p c_{ip}\chi_p \tag{2}$$

Simple LCAO molecular orbitals (Appendix II) have been used in the present work. An electronic state is then given by a linear combination of the appropriate configurations

$$\Psi = A_1\Phi_1 + A_2\Phi_2 + \ldots + A_A\Phi_A + \ldots \tag{3}$$

and the energy E of the state Ψ is found from eq. 4.

$$E = \int \Psi \, \mathcal{3C} \, \Psi \mathrm{d}V \tag{4}$$

In matrix notation, the energy is given by the diagonal elements of the diagonal matrix $\mathbf{E}$, where

$$\mathbf{AHA}^{-1} = \mathbf{E}$$

$\mathbf{A}$ is a unitary matrix and $\mathbf{H}$ is the Hamiltonian matrix with individual matrix elements

$$\mathcal{3C}_{mn} = \int \Phi_m \mathcal{3C} \Phi_n \mathrm{d}V \tag{5}$$

The integrals $\mathcal{3C}_{mn}$ are expressed in terms of core integrals

$$I_{mn} = \int \phi_m^*(1)\mathbf{H}_{core}(1)\phi_n(1)\mathrm{d}V_1 \tag{6}$$

and electronic repulsion integrals

$$(mk|nl) =$$
$$\iint \phi_m^*(1)\phi_n^*(2)(e^2/r_{12})\phi_k(1)\phi_l(2)\mathrm{d}V \tag{7}$$

These molecular integrals are expressed in terms of atomic integrals using eq. 2

$$I_{ij} = \sum_p \sum_q c_{ip}^* c_{jq} H_{pq}^{core} \tag{8}$$

where

$$H_{pq}^{core} = \int \chi_p^*(1)\mathbf{H}_{core}(1)\chi_q(1)\mathrm{d}V_1 \tag{9}$$

The core integrals are then obtained as follows, assuming forma neglect of differential overlap

$$a \equiv H_{pp}^{core} = \int \chi_p^*(1)\mathbf{H}_{core}(1)\chi_p(1)\mathrm{d}V_1 \tag{10}$$

$$\beta \equiv H_{pq}^{core} = \int \chi_p^*(1)\mathbf{H}_{core}(1)\chi_q(1)\mathrm{d}V_1 \tag{11}$$

Employing the ZDO approximation, the electronic repulsion integrals $(ij|kl)$ are obtained as linear combinations of integrals over the atomic orbitals of the form $(pp|qq)$ where

$$\gamma_{pq} \equiv (pp|qq) = \iint \chi_p^*(1)\chi_q^*(2)(e^2/r_{12}) \times$$
$$\chi_p(1)\chi_q(2)\mathrm{d}V_1\mathrm{d}V_2 \tag{12}$$

The key to the success of the method now depends on the empirical evaluation of a_p, β_{pq}, and γ_{pq}, and this evaluation is discussed below. Since we are using Hückel type[11] rather than self-consistent-field molecular orbitals, it is possible to improve the orbitals by configuration interaction among the ground and singly-excited configurations. The configuration interaction treatment has been limited to, and includes all of, the singly excited configurations, together with the ground configuration.

The intensities of the spectral transitions were calculated according to Mulliken and Rieke,[12] simplified by the zero differential overlap approximation. For transitions between nondegenerate states described by wave functions ψ_k and ψ_l, the oscillator strength f is

$$f = 1.085 \times 10^{11}\omega \sum_{i=x,y,z} Q_i^2 \tag{13}$$

where ω is the frequency of the transition in cm.$^{-1}$ and

$$Q_i = \int \Psi_k^* i\Psi_l \mathrm{d}V \ (i = x,y,z) \tag{14}$$

where i is the algebraic sum of the i's for the several electrons.

(11) E. Hückel, *Z. Physik.* **70**, 204 (1931).

(12) R. S. Mulliken and C. A. Rieke, *Rept. Progr. Phys.*, **8**, 231 (1941).

Evaluation of Atomic Integrals and Molecular Orbitals.—The integrals over atomic orbitals to be evaluated are the resonance integrals β_{pq}, the Coulomb attraction integrals α_p, and the Coulomb repulsion integrals γ_{pq}. The atomic orbitals are the nodeless Slater AO's[13]; for the Slater orbital exponent ζ, the empirical value[14] $\zeta_C = 1.59$ was used rather than the theoretical value (1.625).

While it is possible to calculate from the theoretical formula[6] numerical values for the resonance integrals, such a calculation requires that approximations be made concerning the repulsion integrals contained in this formula. Thus there is considerable doubt as to the validity of the "theoretical" value obtained. Furthermore, the theoretical value is a function of the environment of the atom pair considered, and the calculation is tedious. We have therefore followed Pariser and Parr in assuming that the resonance integrals can be taken as constant between a given pair of atoms at a fixed distance, and independent of their environment. We have accepted the numerical value of $\beta = -2.402$ e.v. at 1.397 Å. in benzene, as previously described.[1] For atoms which are not directly bound together, the theoretical formula indicates that β falls off very rapidly with distance, and we have accepted the exponential relationship used previously (15).[1] In principle the values obtained from this formula

$$\beta \text{ (e.v.)} = -61.232e^{-2.31813r \text{ (Å.)}} \tag{15}$$

should be increased slightly to account for $\sigma\sigma$ overlap if the orbitals are not parallel. For the molecules studied here the deviation from planarity is not great enough really to warrant attempting such a refinement for atoms not bound together. For atoms which are bound together, the exponential variation (15) makes β far too dependent on distance. Since it was found necessary to reduce empirically the one- and two-center repulsion integrals considerably below the theoretical value to account for electron correlation, and since the theoretical expression for β contains these integrals,[6] a similar sort of reduction might be expected here. We have therefore elected to use the Mulliken relationship[16] for β between bound atoms (16) where W is an appropriate

$$\beta = {}_{pq}\beta_0 \frac{1/2(W_p + W_q)A_{pq}(S_{pq}/1 + S_{pq})}{W_0A_0(S_0/1 + S_0)} \tag{16}$$

atomic valence state ionization potential, S is the overlap integral, and A is an empirical constant dependent on the type of overlap (1.00 for $S_{\pi\pi}$, and 0.77 for $S_{\sigma\sigma}$). For the present work, since we are considering only double bonds between carbon atoms and using benzene as our standard, this reduces to

$$\beta_{pq} \text{ (e.v.)} = -11.712\frac{S_{\pi\pi}}{1 + S_{\pi\pi}} \tag{17}$$

Coulomb Attraction Integrals.—In terms of atomic orbitals the theoretical expression for the one-center Coulomb attraction integral α is

$$\alpha_p = W_p - \sum_{p \neq q} [(pp|qq) + (q:pp)] - \sum_r (r:pp) \tag{18}$$

where $(pp|qq)$ are the Coulomb repulsion integrals γ_{pq}, and $(q:pp)$ and $(r:pp)$ are Coulomb penetration integrals between χ_p and neutral atoms q and r. These latter terms are small $[(q:pp) \cong 0.1\gamma_{pq}$ for p and q neighbors, much less for p,q nonneighbors], and have little effect on the calculated spectrum of an all carbon system. Neglecting penetration integrals, the α's are obtained from

$$\alpha_p \text{ (e.v.)} = -11.22 - \sum_{p \neq q} \gamma_{pq} \tag{19}$$

Coulomb Repulsion Integrals.—These integrals are available directly from tables,[16] and if the π-orbitals are not parallel, they should be factored into π, $\bar{\pi}$, and σ components. At distances

(13) J. C. Slater, *Phys. Rev.*, **36**, 57 (1930).

(14) R. G. Parr and B. L. Crawford, Jr., *J. Chem. Phys.*, **16**, 526 (1948).

(15) (a) R. S. Mulliken, *J. Am. Chem. Soc.*, **72**, 4493 (1950); (b) *J. Phys. Chem.*, **56**, 295 (1952).

(16) R. C. Sahni and J. W. Cooley, "Tables for Two-center Two-electron Coulomb Integrals," National Aeronautics and Space Administration Technical Note D-146-II, Washington, D. C., 1960.

of less than 2.408 Å. it is necessary to reduce the theoretical values empirically in order to account for electron correlation. This was done earlier following the method suggested by Schiess and Pullman.[8] The equation obtained[1] was

$$\gamma_{pq} \text{ (e.v.)} = 11.080 - 3.92327r +$$
$$0.69786r^2 \quad (r \le 2.408 \text{ Å}) \quad (20)$$

No attempt has been made to factor repulsion integrals at these close distances since the empirical curve is so arbitrary as it is.

Computer Programs.—The calculations were done on an IBM 7070 computer using programs written in Fortran II (Full Fortran). The program sequence begins with the diagonalization of the matrix given in Appendix II. The resulting eigenvectors, arranged in order of decreasing eigenvalue, are the MO coefficients c_{ip}. These, together with the matrices Γ and H_{core}, are the input data for a series of programs which calculate in order the quantities in eq. 8, 21–28.[7]

$$I_i = \sum_{p,q\,=\,1}^{n} c_{ip} c_{iq} H_{pq}^{core} \quad (8)$$

$$J_{ij} = \sum_{p,q} c_{ip} c_{ip} c_{jq} c_{jq} \gamma_{pq} \quad (21)$$

$$K_{ij} = \sum_{p,q} c_{ip} c_{iq} c_{jp} c_{jq} \gamma_{pq} \quad (22)$$

$$V_0 = 2\sum_{i\,=\,1}^{f} I_i + \sum_{i,j}(2J_{ij} - K_{ij}) + \sum_{p\,>\,q} \gamma_{pq} \quad (23)$$

$$V_{ik} = V_0 + I_k - I_i + J_{ik} + K_{ik} - J_{ii} -$$
$$\sum_{f\,\neq\,i}(2J_{fi} - 2J_{fk} - K_{fi} + K_{fk}) \quad (24)$$

The subscript f in (23) and (24) refers to orbitals which are doubly occupied in the ground state. (V_0 is corrected for internuclear repulsion energy by the third summation in eq. 23.)[17a]

$$\langle V_0 | V_{ik} \rangle = 2^{1/2} \Big\{ I_{ik} + (ii|ik) +$$
$$\sum_{f\,\neq\,i,k}[2(ff\,ik) - (fi\,fk)] \Big\} \quad (25)$$

The electronic integrals are evaluated as above, e.g.,

$$(12|34) = \sum_{p,q} c_{1p} c_{2p} c_{3q} c_{4q} \gamma_{pq}$$

$$\langle V_{ik} | V_{jk} \rangle = -I_{ij} + 2(ik|jk) - (ij|ii) - (ij|kk) -$$
$$(ij|jj) - \sum_{f\,\neq\,i,j}[2(ff|ij) - (fi|fj)] \quad (26)$$

$$\langle V_{ik} | V_{jl} \rangle = 2(ik|jl) - (ij|kl) \quad (27)$$

$$\langle V_{ik} | V_{il} \rangle = I_{kl} + (ik|il) + (ii|kl) +$$
$$\sum_{f\,\neq\,k,l,i}[2(ff|kl) - (fk|fl)] \quad (28)$$

The configuration energies and configuration interaction matrix elements are then arranged to give the Hamiltonian matrix H, which is diagonalized to give the state energies (eigenvalues) and the configuration coefficients $A_{a;k}$ (eigenvectors). The oscillator strengths (eq. 13) are evaluated according to the method given by Pariser[7] from the state energies, configuration coefficients, molecular orbitals, and nuclear coordinates.

Discussion

The calculated benzene spectrum[1] was adjusted empirically to fit the observed spectrum, so the agreement between the two is quite good. Since there are a number of empirical adjustments which could have been made which would have given a satisfactory calculated benzene spectrum, there is no guarantee that it will be possible to fit results for other compounds of interest using the same methods and numerical quantities as used for benzene. There are, moreover, additional

factors peculiar to the different compounds which are not encountered in the benzene system, and which may be taken into account in varying ways. The inclusion of resonance integrals only between neighbors, for example, is not a clear cut concept in compounds such as norbornadiene. Thus for the sake of selfconsistency, we decided to omit resonance integrals between nonneighbors in the conjugated systems, but to include them (evaluated by the exponential formula) for those nonconjugated systems where the internuclear distances are between the benzene 1,3- and 1,4-distances.

The method of evaluating data described above appears to us to be the most logical, but other possibilities were also examined: for example, for *trans*-butadiene the exponential formula was used to evaluate β_{12} and β_{23}, with the other β's being set equal to zero. The results were quite unsatisfactory. When the Mulliken relationship was used for all resonance integrals (β_{12}, β_{23}, β_{13}, and β_{14}), the value for the low energy transition was satisfactory, but the second transition was in poor agreement with experiment. All of the pertinent numerical information is summarized in Appendices I and II.

The results of the calculation for butadiene as a function of the dihedral angle about the 2,3-bond are presented in Table I. Certain features of interest from the calculations can be seen in this table, as follows: the *cis* isomer should show absorption at longer wave length (230 mμ) than the *trans* (212 mμ), and this absorption should be only about half as intense as that of the *trans*. As the dihedral angle at the 2,3-bond changes from 0 to 90° to 180° the wave length of the N → V$_1$ absorption drops from 230 to 182 and then rises to 212 mμ. At the same time the oscillator strength goes from 0.5 to 0 to 1. The qualitative features calculated here are in good agreement with those observed from a study of more complicated systems containing butadiene structures with various 2,3-dihedral angles.

TABLE I

CALCULATED TRANSITION ENERGIES AND OSCILLATOR STRENGTHS FOR BUTADIENE (II) AS A FUNCTION OF THE DIHEDRAL ANGLE

Dihedral angle θ, deg.	N → V$_1$ λ, mμ	f	N → V$_2$ λ, mμ	f	N → V$_3$ λ, mμ	f	N → V$_4$ λ, mμ	f
0	230	0.465	182	0.044	161	0.703	133	10^{-4}
30	210	.463	182	.040	164	.664	137	0.021
60	201	.392	183	.015	167	.571	154	.159
85	183	.089	182	.001	170	.429	170	.601
90	182	.000	182	.000	170	.394	170	.725
95	183	.091	181	.001	171	.358	169	.673
120	195	.581	180	.019	172	.171	150	.391
150	204	.908	179	.017	171	.031	134	.292
180	212	.997	179	.000	170	.000	129	.292

A study of the ground state of butadiene ($\theta = 0$, 90, and 180°) by the SCF method was carried out recently[17b] and complements the present work. The methods and numerical values used in the two studies were quite different, yet conclusions from the point of overlap between them (the variation of the energy of the π-system with θ) are similar, namely that the *s-cis-* and

(17) (a) R. G. Parr and R. Pariser, *J. Chem. Phys.*, **23**, 711 (1955); (b) I. Fischer-Hjalmars, paper presented at the Winter Institute in Quantum Chemistry and Solid State Physics, Sanibel Island, Fla., Jan., 1962. The authors are indebted to Dr. Fischer-Hjalmars for a preprint of this paper.

s-trans systems have similar π-energies, while the perpendicular form is some 10 kcal./mole higher.

Recently the synthesis of 2,3-di-*t*-butyl-1,3-butadiene (VIII) was reported.[18] Due to the steric requirements of the *t*-butyl groups, it was expected that this com-
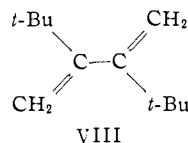
VIII

pound would exist in the twisted form, corresponding to θ equals 90°. Nuclear magnetic resonance studies confirmed this conformation. In the vapor phase, VIII was reported to show a shoulder at 209 mμ and the major peak at 185 mμ in good agreement with our calculated value of 182 mμ for 90°-II. (The shoulder at 209 was attributed to characteristic absorption of substituted ethylenes.[19] Alternatively, it might be due to the presence of a small amount of a transoid conformation.)

The calculated oscillator strength for *trans*-butadiene appears to be too large by about a factor of 3, but the ratios of the oscillator strengths as a function of dihedral angle appear to be about right. Since the oscillator strength is quite a sensitive function of the electron distribution,[20] it is expected that there may be appreciable quantitative errors here, and the agreement is regarded as satisfactory. The agreement between the calculated and experimental[21] values for the *s-trans* isomer is excellent, both for the N → V_1 and N → V_2 transitions: N → V_1, calcd. 212, exptl. 209.4; N → V_2, calcd. 175, exptl. 175.4. Since butadiene actually exists in the *s-trans* conformation, the spectrum of the *s-cis* conformer is not known. (There is experimental evidence[22] which indicates that 3–7% of *cis*-II may be present at room temperature, but no ultraviolet absorption has been attributed to it.)

While the electronic spectrum of butadiene itself for θ ≠ 180° is not known, there are a number of substituted cisoid dienes available for comparison purposes. The N → V_1 transition energies have been reported for cyclopentadiene, cyclohexadiene, cycloheptadiene, cyclooctadiene, and cyclononadiene. The spectra were measured in various solvents, and such values are generally found to be about 10 mμ higher than in the vapor phase.[23] From an examination of scale models it is possible to make a rather good estimate of the dihedral angle between the olefinic linkages for each of these compounds except the last.[24] For each of these angles then, one can estimate by interpolation of the data in Table I where the butadiene linkage should absorb. The presence of the two methylene groups on the ends of the butadiene system will raise the value 10 mμ above that which would be observed in the butadiene itself, and another 10 mμ is added as a solvent correction. The calculated values thus obtained are listed in Table

II and compared with the experimental values for these compounds. It is noted that the calculated wave lengths for the cisoid dienes tend to be rather consistently about 12 mμ lower (0.24 e.v. higher) than those observed, with the exception of cyclopentadiene.

Compound	θ,[25] deg.	$\lambda_{m\mu}$[26] (calcd.)	$\lambda_{m\mu}$ (exptl.)	Ref.
s-trans-Butadiene	180	212[27]	209.4[27]	21
1,3-Cyclopentadiene	0	250	242	28
1,3-Cyclohexadiene	17	245	256.5	29
1,3-Cycloheptadiene	52	230	248	29
1,3-Cyclooctadiene	64	216	229	30
1,3-Cyclononadiene.	65	216	219.5	31
nonrigid, various possibili-	90	202		
ties from 65–110°	110	211		

The transitions from the ground state to the two triplet states of lowest energy were also calculated for *cis*- and *trans*-II and for IIIa, and are compared with observed values[32] in Table III. The agreement here is rather poor, but since the empirically evaluated quantities used in the calculation were obtained from transitions to singlet states, this is not surprising.[33] Hammond's work[34] on the dimerization of dienes in the triplet state strongly suggests that the lowest triplet state should be lower for *s-cis*-butadiene than it is for the *s-trans* conformer, although cyclohexadiene itself is not an ideal model for the *cis* conformer. The energies calculated here are the same for the two conformers, but these values are of limited accuracy for reasons mentioned.

TABLE III

CALCULATED AND OBSERVED TRIPLET TRANSITION ENERGIES

System	Transition	Energy, e.v. Calcd.	Obsd.
cis-II	N → T_1	2.26	3.0[a]
	N → T_2	3.87	..
trans-II	N → T_1	2.22	3.22
	N → T_2	3.82	3.84
IIIa	N → T_1	1.84	2.58
	N → T_2	3.18	3.22

[a] This value is estimated from the value of cyclohexadiene (2.85 e.v. (ref. 32)) which must be corrected for nonplanarity and for substitution.

1,3-*trans*,5-Hexatriene (2-*s-cis*; 4-*s-trans*).—Both the liquid[35,36] and vapor phase[37,38] spectra of this compound have been reported. Fine structure is observed

(18) H. Wynberg, A. DeGroot, and D. W. Davies, *Tetrahedron Letters*, 1083 (1963).

(19) R. S. Berry, *J. Chem. Phys.*, **38**, 1934 (1963).

(20) C. M. Moser, *J. Chem. Soc.*, 3455 (1954).

(21) L. C. Jones, Jr., and L. W. Taylor, *Anal. Chem.*, **27**, 228 (1955).

(22) W. B. Smith and J. L. Massingill, *J. Am. Chem. Soc.*, **83**, 4301 (1961).

(23) Vapor phase spectra for some of the dienes are available: cyclohexadiene, 250 mμ (ref. 37); cyclopentadiene, 235 mμ; and cyclooctadiene, 222 mμ (ref. 28).

(24) E. A. Braude, *Chem. Ind.* (London), 1557 (1954).

(25) Measured from Dreiding models, accurate to ±5°.

(26) These values are calculated for solution in hexane (see text).

(27) Vapor phase.

(28) Present work (in hexane solvent); ref. 25 gives 238.5 mμ.

(29) S. F. Mason, *Quart. Rev.* (London), **15**, 287 (1961).

(30) A. C. Cope, M. R. Kinter, and R. T. Keller, *J. Am. Chem. Soc.*, **76**, 2757 (1954).

(31) R. W. Fawcett and J. O. Harris, *J. Chem. Soc.*, 2669 (1954).

(32) D. F. Evans, *ibid.*, 1735 (1960).

(33) The empirical reduction of the value of the one- and two-center repulsion integrals at short distances, for example, is a way of including the effect of electron correlations in the calculation. This correlation should be different for the triplet states, however.

(34) G. S. Hammond and R. S. H. Liu, *J. Am. Chem. Soc.*, **85**, 477 (1963).

(35) J. M. Shackelford, W. A. Michalowicz, and L. H. Schwartzman, *J. Org. Chem.*, **27**, 1631 (1962).

(36) J. C. H. Hwa, P. L. de Benneville, and H. J. Sims, *J. Am. Chem. Soc.*, **82**, 2537 (1960).

(37) H. Schuler, E. Lutz, and G. Arnold, *Spectrochim. Acta*, **17**, 1043 (1961).

(38) W. C. Price and A. D. Walsh, *Proc. Roy. Soc.* (London), **A185**, 182 (1946).

TABLE IV

CALCULATED AND OBSERVED SPECTRA OF CONJUGATED TRIENES

| Compound	λ_{max}, mμ. obsd.	Ref.	λ, mμ^a	ε	Triene system	Calculated transitions					
						N → V$_1$		N → V$_2$		N → V$_3$	
						λ, mμ	f	λ, mμ	f	λ, mμ	f
IIIa (vapor)	241.2	36	241.2	....	IIIa	244	1.461	201	0.000	182	0.062
	175		175	....							
IIIa	256	35	241	48,000							
X	269	39	234	....							
XI	284	39	239	....							
IIIb	255	36	240	41,000	IIIb	241	1.275	205	0.021	187	0.062
Ergosta-4,6,8(14),22-tetraene	283	40	238	33,000							
Cholesta-2,4,6-triene	306	40	271	15,700	IIIc	254	0.844	199	0.070	184	0.205
Cholesta-3,5,7-triene	315	40	270	15,700							
Tachysterol	281	42	241	26,400							
	280	41	240	29,300							
Androsta-5,7,9(11)-triene-3β,17β-diol	324	32	284	12,680	IIId	266	0.473	215	0.010	192	0.689
Vitamin D$_2$	265	32b	230	18,300							
Cholesta-4,6,8,11-tetraen-3β-ol	355	32	285	13,500	IIIe	264	0.714	203	0.000	198	0.000
Cholesta-6,8(14),9(11)-triene 3β-acetate	285	32	245 (230)	9,100	IX	244	0.342	213	0.000	205	0.862
	243		203 (188)	12,100							

^{a} The value for the stripped chromophore calculated from the observed value.

due to vibrational transitions. The center of gravity of the next to the longest wave length band (which is also the band of maximum extinction) occurs at 242 mμ in the vapor phase and is taken as the transition energy for present purposes. The calculated value is in very good agreement with that observed. The oscillator strength is much greater than that of butadiene, as calculated. There are in addition to the above conformation IIIa four other planar conformations for the isomers of this molecule which are possible in principle: 1,3-*cis*,5-hexatriene(2-*s-trans*; 4-*s-trans*) (IIIb), 1,3-*trans*,5-hexatriene (2-*s-cis*; 4-*s-trans*) (IIIc), 1,3-*cis*,5-hexatriene (2-*s-cis*; 4-*s-trans*) (IIId), and 1,3-*trans*,5-hexatriene (2-*s-cis*; 4-*s-cis*) (IIIe). While we do not expect to find significant amounts of these conformations present in this molecule under ordinary circumstances, they are electronic systems of types which we may expect to find in polycyclic molecules. The calculations have therefore been carried out for each of these conformations, and the results are summarized in Table IV. System IX, a typical cross-conjugated triene, was also examined.
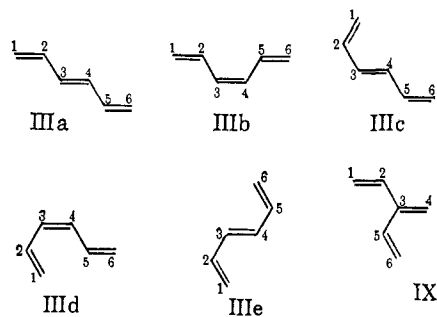
Comparison of the calculated values in Table IV with experiment is necessarily indirect: while relatively simple systems (X, XI) with the triene confor-

(39) H. H. Inhoffen and G. Quinkert, *Ber.*, **87**, 1418 (1954).

(40) L. Dorfman, *Chem. Rev.*, **53**, 47 (1953).

(41) R. S. Davidson, P. S. Littlewood, T. Medcalfe, S. M. Waddington-Feather, D. H. Williams, and B. Lythgoe, *Tetrahedron Letters*, **21**, 1413 (1963).

(42) Reference 5, p. 145.

(43) Reference 5, p. 133.

mation of IIIa are known, in addition to IIIa and IIIb themselves, the only molecules containing the other conformations which are available for comparison with
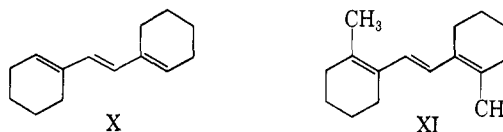
experiment are complicated systems (mostly steroids) which contain other features in addition. The compounds judged to be the most closely related to the systems for which the calculations have been made and for which spectral data are available are listed in Table IV together with the wave length and extinction coefficient of the major observed maximum. To facilitate comparison with the calculated values, the "stripped chromophore" value for the basic polyene structure is obtained by subtracting from the observed maximum wave length increments according to Woodward's rules. From the wave length thus obtained, an additional 15 mμ is subtracted to convert from solvent to the gas phase. These values are given as the "experimental" wave lengths in Table IV.

Comparison of the calculated and observed values in Table IV supports the conclusion drawn above for the dienes, *i.e.*, that the calculated absorption wave length for each *cis*-diene system is too low by an amount corresponding to about 0.24 e.v. (about 14 mμ). Again the agreement is excellent for the all-*trans* systems, and the addition of 14 mμ per *cis*-diene group (1 each in IIIc, IIId, and IV, 2 in IIIe) to the calculated values would bring the remaining systems into satisfactory agreement with experiment. The calculated oscillator strengths are also in generally good qualitative agreement with the observed extinction coefficients.

In the case of the cross-conjugated system IX, comparison with experiment is difficult, since the stripped chromophore value is questionable. The figures outside parentheses were obtained by correcting the observed value for solvent and substituents only; those inside parentheses are the observed value corrected

according to Woodward's rules, which are not really applicable here. The agreement of the former with the calculated values is probably fortuitous.

The stripped chromophore values of tachysterol and of vitamin D_2 appear anomalous, disagreeing with both the calculated values and similar "observed" values and extinction coefficients. This disagreement can be accounted for in both cases, however. Considering the exocyclic double bond structure of vitamin D_2, the low value of the "observed" wave length can most readily be attributed to nonplanarity of the cisoid diene system. This has in fact been experimentally deter-

| vitamin D_2 | X | IIId | androstra-5,7,9(11)-triene |
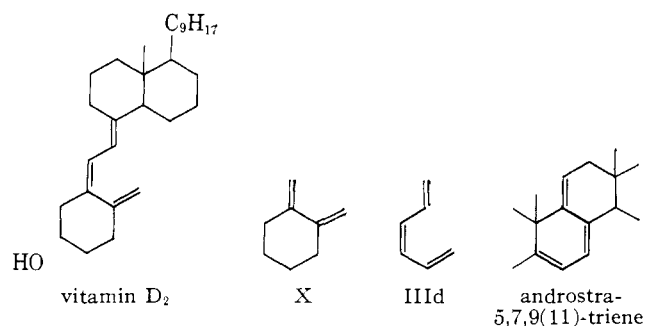
mined by X-ray analysis.[44] From models, the non-planarity of a similar system, X, is about 40° (the system is rather flexible), and the observed vapor phase wave length[28] is 212 mμ (calculated from Table I adding 10 mμ for substituents, 222 mμ). The addition of a double bond extending conjugation should raise the value to 232 mμ, which agrees with the corresponding value for vitamin D_2, 230 mμ. In the corresponding steroidal triene the geometry of the double bonds is fixed and essentially planar; and the "observed" value agrees well with that calculated for the planar IIId system.

In tachysterol, commonly written as A,[41,45] the stereochemistry of the triene system was assumed to be that of IIIc on the basis of spectral evidence indicating a 3,4-*trans* configuration,[45] and the high degree of reactivity in the addition of citaconic anhydride.[46] This stereochemistry appears to have been generally

| A | B | IIIc | IIIa |

tachysterol
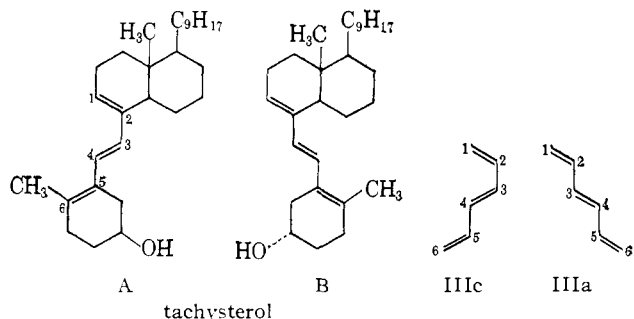
accepted,[41,42] but interpreting the experimental evidence on the basis of the present work, this assignment of the 1,2;3,4 system as cisoid is doubtful. First of all, if the calculated value for IIIc is increased to 268 mμ (correcting for the systematic *cis*-diene error), the agreement with the "observed" spectra of the cholestatrienes, whose triene systems are unambigously IIIc, is

quite good. But the corresponding value for tachysterol, 241 mμ, is now considerably farther from agreement than indicated in Table III, and in fact the disagreement between these values is so severe that it is concluded that tachysterol does not have the conformation assigned earlier. If, however, the 3,4-configuration is *trans*, the observed spectrum is in excellent agreement with that calculated for IIIa. The ease of Diels–Alder addition, dependent on the energy difference between the ground and transition states of the molecule, cannot be taken as evidence against the IIIa system.

If the 3,4-configuration in tachysterol were *cis*, models indicate that severe steric repulsions would force one of the terminal olefinic groups to rotate close to 90° out of conjugation. The observed transition wave length is consistent with either a 1,2;3,4- or 3,4;5,6-cisoid conjugated diene system. (For the comparable 3,4-*cis*-triene synthesized by Inhoffen, *et al.*,[39] the corrected experimental value is 218 mμ, similar to a *trans*-conjugated diene system.) Such a *cis*-conjugated diene with the adjacent double bond rotated out of conjugation is also consistent with the observed wave length, but can be ruled out due to the high value of the observed extinction coefficient. It is therefore suggested that tachysterol should be represented not as A, but as B.

Unconjugated Systems.—A number of polyenes are known in which the double bonds are unconjugated in a formal sense, and yet are spatially close enough to interact, as evidenced from their ultraviolet spectra. As typical examples of this kind of structure, we have selected norbornadiene (IV) and barrelene (V).

The interactions between such systems have been treated as charge transfer interactions,[47,48] but they require no special treatment within the Pariser–Parr framework, where they are treated just as the conjugated polyenes, the only difference being in the numerical values which are used for the integrals involved.

TABLE V

CALCULATED AND OBSERVED SPECTRA OF NORBORNADIENE (IV) AND BARRELENE (V)

Compound	Transition	Calculated		Observed	
		λ, mμ	f	λ, mμ	log ε
IV	N → V_1	211	0.000	211[10]	~2.9[9]
	N → V_2	196	.001	188[10]	~3.2[9]
V	N → V_1	214	.000	224[a]	2.48
	N → V_2	194	.056	198[a]	3.05

[a] Corrected to gas phase.

TABLE VI

CALCULATED AND OBSERVED SPECTRA OF CYCLONONATRIENE (VI) AND UMBRELLAENE (VIII)

Compound	Calculated		Observed[a]	
	λ, mμ	f	λ, mμ	log ε
VI	205	3 × 10⁻⁵	~216 (sh)	>3
	171	0.000	212 (sh)	3
	168	0.452	198	4
	164	1.318	<190	Strong
VII	216	0.000	204 (sh)	3.7
	178	0.000	187	4.4
	174	1.013		
	170	0.910		

[a] In solvent.

(44) D. Crowfoot and J. D. Dunitz, *Nature*, **162**, 608 (1948); D. C. Hodgkin, M. S. Webster, and J. D. Dunitz, *Chem. Ind.*, (London), 1149 (1957).

(45) H. H. Inhoffen, K. Bruckner, R. Grundel, and G. Quinkert, *Ber.*, **87**, 1407 (1954).

(46) K. Alder and M. Schumacher, *Fortschr. Chem. Org. Naturstoffe*, **10**, 74 (1953).

(47) H. C. Longuet-Higgins and J. N. Murell, *Proc. Phys. Soc.* (London), **A68**, 601 (1955).

(48) J. Koutecky and J. Paldus, *Tetrahedron, Suppl.* **2**, 201 (1963).

TABLE VII

MOLECULAR ORBITALS

θ		χ_1	χ_2	χ_3	χ_4	χ_5	χ_6
II 0° and 180°	ϕ_1	0.407394	0.577953	0.577953	0.407394		
	ϕ_2	− .577953	− .407394	.407394	.577953		
	ϕ_3	− .577953	.407394	.407394	− .577953		
	ϕ_4	− .407394	.577953	− .577953	.407394		
II 30° and 150°	ϕ_1	.405218	.579481	.579481	.405218		
	ϕ_2	− .579481	− .405218	.405218	.579481		
	ϕ_3	− .579481	.405218	.405218	− .579481		
	ϕ_4	− .405218	.579481	− .405218	.579481		
II 60° and 120°	ϕ_1	.445264	.549308	.549308	.445264		
	ϕ_2	− .549308	− .445264	.445264	.549308		
	ϕ_3	− .549308	.445264	.445264	− .549308		
	ϕ_4	− .445264	.549308	− .549308	.445264		
II 85° and 95°	ϕ_1	.490926	.508912	.508912	.490926		
	ϕ_2	− .508912	− .490926	.490926	.508912		
	ϕ_3	− .508912	.490926	.490926	− .508912		
	ϕ_4	− .490926	.508912	− .508912	.490926		
II 90°	ϕ_1	.500000	.500000	.500000	.500000		
	ϕ_2	− .500000	− .500000	.500000	.500000		
	ϕ_3	− .500000	.500000	.500000	− .500000		
	ϕ_4	− .500000	.500000	− .500000	.500000		
IIIa–e	ϕ_1	.250133	.409300	.519525	.519525	0.409300	0.250133
	ϕ_2	− .443755	− .515720	− .192650	.192650	.515720	.443755
	ϕ_3	.490423	.257887	− .439294	− .439294	.257887	.490423
	ϕ_4	− .490423	.257887	.439294	− .439294	− .257887	.490423
	ϕ_5	.443755	− .515720	.192650	.192650	− .515720	.443755
	ϕ_6	− .250133	.409300	− .519525	.519525	− .409300	.250133
IV	ϕ_1	.500000	.500000	.500000	.500000		
	ϕ_2	− .500000	− .500000	.500000	.500000		
	ϕ_3	− .500000	.500000	.500000	− .500000		
	ϕ_4	− .500000	.500000	− .500000	.500000		
V	ϕ_1	.351469	.351469	.572411	.572411	−0.220942	−0.220942
	ϕ_2	.458043	.458043	− .075360	− .075360	.533402	.533402
	ϕ_3	− .408248	− .408248	.408248	.408248	.408248	.408248
	ϕ_4	− .553204	.553204	.419689	− .419689	− .133515	.133515
	ϕ_5	− .165222	.165222	− .396478	.396478	− .561700	.561700
	ϕ_6	− .408248	.408248	− .408248	.408248	.408248	− .408248
VI	ϕ_1	.408248	.408248	.408248	.408248	.408248	.408248
	ϕ_2	− .205367	− .245146	− .364616	− .330117	.469982	.575262
	ϕ_3	− .439590	− .522721	.447648	.473662	.091942	.049058
	ϕ_4	.510458	− .488855	− .488841	.510445	− .021617	− .021591
	ϕ_5	.269752	− .307172	.307194	− .269776	− .576945	.576946
	ϕ_6	− .408248	.408248	− .408248	.408248	− .408248	.408248
VII	ϕ_1	.408248	.408248	.408248	.408248	.408248	.408248
	ϕ_2	− .318563	− .357554	− .257718	− .213800	.576280	.571352
	ϕ_3	− .481509	− .453309	.516638	.536305	− .035129	− .082996
	ϕ_4	.511603	− .487545	− .487527	.511588	− .024077	− .024043
	ϕ_5	.267574	− .309247	.309275	− .267603	− .576847	.576849
	ϕ_6	− .408248	.408248	− .408248	.408248	− .408248	.408248
IX	ϕ_1	.249041	.433565	.613153	.352197	.433565	.249041
	ϕ_2	− .500000	− .500000	.000000	.000000	.500000	.500000
	ϕ_3	− .433565	− .249041	.352197	.613153	− .249041	− .433565
	ϕ_4	.433565	− .249041	− .352197	.613153	− .249041	.433565
	ϕ_5	− .500000	.500000	.000000	.000000	− .500000	.500000
	ϕ_6	− .249041	.433565	− .613153	.352197	.433565	− .249041

Norbornadiene has previously been treated by the Pariser–Parr method,[9,10] but with different numerical values for the various quantities. We have obtained numerical quantities for this molecule by the methods described above. The results obtained were in good agreement with the observable portion of the spectrum (Table V). The calculation was next extended to bicyclo[2.2.2]-2,5,7-octatriene (barrelene).[49] This system is unusual in that the signs of the overlap integrals must be taken into account. Owing to the peculiar

orientation of the π-orbitals, there is no combination of the atomic orbitals which will give a nodeless molecular orbital, and the MO of lowest energy is found to be degenerate, which is also unusual. The calculated values for the N → V_1 and N → V_2 transitions are given in Table V. The only experimental values for the spectrum which are available give the wave lengths as 239 and 208 mμ in ethanol. In the vapor phase these values would probably be reduced to about 224 and 198 mμ, so the agreement appears to be satisfactory.

The homoconjugated compound tetrahydroacepentylene (umbrellaene, VII) has long been of theoret-

(49) H. E. Zimmerman and R. M. Paufler, J. Am. Chem. Soc., 82, 1514 (1960).

TABLE VIII

STATE ENERGIES, TRANSITION ENERGIES, AND OSCILLATOR STRENGTHS[a]

State	I −E, e.v.	ΔE, e.v.	f	IIIa −E, e.v.	−E, e.v.	f	IIIb −E, e.v.	ΔE, e.v.	f	III −E, e.v.	ΔE, e.v.	f
V_0	80.02	0.00	0.000	87.21	0.00	...	78.63	0.00		79.41	0.00	...
V_{34}	73.32	6.70	1.441	82.13	5.08	1.461	73.49	5.14	1.275	74.54	4.87	0.844
V_{35}	73.32	6.70	1.145	80.35	6.86	0.000	72.59	6.04	0.021	73.19	6.22	.070
V_{36}	71.49	8.53	0.000	80.40	6.81	.062	71.74	6.89	.047	71.93	7.48	.485
V_{24}	75.24	4.79	.000	81.05	6.16	.000	71.99	6.64	.062	72.67	6.74	.205
V_{25}	74.03	5.99	.000	78.14	9.07	.307	69.88	8.75	.264	69.98	9.48	.014
V_{26}	71.49	8.53	.000	78.18	9.03	.000	68:37	10.26	.034	68.56	10.76	.006
V_{14}	71.69	8.33	.000	79.96	7.25	2×10^{-4}	71.54	7.09	.044	72.46	6.96	.003
V_{15}	71.69	8.33	.000	76.52	10.69	0.000	69.48	9.15	.145	70.26	9.15	.353
V_{16}	68.49	11.53	.000	75.91	11.30	0.142	67.58	11.05	.120	68.31	11.10	.051

State	IIId −E, e.v.	ΔE, e.v.	f	IIIe −E, e.v.	ΔE, e.v.	f	V −E, e.v.	ΔE, e.v.	f	State	IV −E, e.v.	ΔE, e.v.	f
V_0	78.50	0.00	...	78.33	0.00	...	76.50	0.00	...	V_0	50.45	0.00	...
V_{34}	73.85	4.65	0.473	73.64	4.69	0.714	70.71	5.79	0.000	V_{23}	44.58	5.87	0.000
V_{35}	72.05	6.45	.689	72.21	6.12	.000	70.71	5.79	.000	V_{24}	44.13	6.32	.001
V_{36}	71.10	7.40	.442	71.55	6.78	.000	70.10	6.40	.056	V_{13}	43.21	7.24	.011
V_{24}	72.75	5.75	.010	72.06	6.27	.000	69.60	6.90	.000	V_{14}	43.58	6.87	.000
V_{25}	70.25	8.25	.062	69.51	8.82	.025	68.42	8.08	1.920				
V_{26}	69.61	8.89	.166	68.11	10.22	.000	69.21	7.29	0.000				
V_{14}	71.63	6.87	.003	70.71	7.62	1.143	69.63	6.87	.000				
V_{15}	68.94	9.56	.003	69.47	8.86	0.000	69.63	6.87	.000				
V_{16}	67.98	10.52	.065	67.59	10.74	0.011	69.21	7.29	.000				

State	VI −E, e.v.	ΔE, e.v.	f	VII −E, e.v.	ΔE, e.v.	f	IX −E, e.v.	ΔE, e.v.	f
V_0	76.52	0.00	...	75.68	0.00	...	78.23	0.00	...
V_{34}	69.12	7.40	0.228	68.55	7.13	0.228	73.14	5.09	0.341
V_{35}	69.25	7.27	.000	68.70	6.98	.000	72.17	6.06	.826
V_{36}	68.81	7.71	.000	68.22	7.46	.000	70.88	7.35	.273
V_{24}	69.12	7.40	.224	68.55	7.13	.228	72.40	5.83	.000
V_{25}	70.48	6.04	3×10^{-6}	69.94	5.74	.000	70.39	7.84	.088
V_{26}	68.94	7.58	0.656	68.37	7.31	.630	69.03	9.20	.000
V_{14}	68.94	7.58	.662	68.37	7.31	.630	70.97	7.26	.000
V_{15}	68.81	7.71	.000	68.22	7.46	.000	69.39	8.84	.377
V_{16}	68.60	7.92	.000	68.00	8.68	.000	67.36	10.87	.021

[a] These data for II are given in Table I.

ical interest, and we carried out the calculations for this molecule with the hope that it might be prepared in the future. Subsequently we learned that a synthesis of the compound has actually been accomplished and the experimental spectrum was obtained.[50] The data are summarized in Table VI. The synthesis of *sym-cis,-cis,cis*-1,4,7-cyclononatriene (VI) was reported while these calculations were in progress,[51,52] and because of its close similarity to umbrellaene we also carried out the calculations for this molecule. The results are again included in Table VI. It is difficult to decide whether the agreement between the calculated and observed spectra is good or not, since there appears to be much vibrational structure in the observed spectrum. All that can be said is that no conspicuous disagreement is apparent.

It is concluded that for polyenes which do not possess strongly allowed transitions above 200 mμ, calculations such as those in this paper will be of limited predictive value. For other polyenes useful predictions will be possible, subject to certain limitations. The most conspicuous limitation is that *cisoid* dienes absorb systematically at longer wave lengths than calculated, possibly because their geometry is not quite that assumed, or because of the neglect of diexcited and higher configurations in the configuration interaction

calculation. Woodward's rules, while of considerable empirical use in their area of applicability. have a number of theoretical shortcomings, and appear to work as well as they do because of internal compensating errors. The triplet state calculations leave much to be desired. All of these matters are of practical importance and are now under investigation and will be reported in subsequent papers.

Appendix I

Molecular Geometry.—The molecules considered were placed in a three-dimensional cartesian coordinate system. Known bond lengths and angles were used where available.

I^{53} $r_{12} = 1.397$ Å.   C—C—C $= 120°$

II^{54} $r_{12} = 1.337$ Å.   C=C—C $= 122.4°$

   $r_{23} = 1.483$ Å.

IV^9 $r_{12} = 1.333$ Å. C_1—C_2—$C_3 = 109.1°$

   $r_{15} = 1.522$ Å. C_1—C_5—$C_7 = 96.4°$

   $r_{67} = 1.558$ Å. C_1—C_5—$C_4 = 102.2°$

(50) R. B. Woodward and T. Fukunaga, unpublished (personal communication).

(51) P. Radlick and S. Winstein, *J. Am. Chem. Soc.*, **85**, 344 (1963).

(52) K. G. Untch, *ibid.*, **85**, 345 (1963).

(53) A. Almenningen, O. Bastiansen, and L. Fernholt, *Kgl. Norske Videnskab. Selskabs Skrifter*, **No. 3**, 1 (1958).

(54) (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).

Where the geometry is not accurately known, standard bond lengths and angles were used.

IIIa   Bond lengths and angles of II

IIIb–e Bond lengths of II, C=C—C = 120°

V r_{12} = 1.337 Å.

        r_{18} = 1.501 Å.[55]

        r_{23} = 2.375 Å. (measured from Dreiding models)

VI r_{23} = 1.337 Å.   C=C—C = 120°

        r_{17} = 1.501 Å.   C—C—C = 109°28'

VII   Average measured Dreiding model distances were used. The coordinates were calculated from various groups of measured distances until consistency between calculated and measured values was achieved

IX   Bond lengths of II, C=C—C = 120°

Appendix II

Numerical Data.—Selected numerical data for the calculated spectra are given in Tables VII and VIII.[56] Molecular orbitals were obtained by diagonalizing ma-

(55) D. R. Lide, Jr., *Tetrahedron*, **17**, 125 (1962).

(56) These data for I have been published previously (ref. 1). For the other compounds treated in this paper the nuclear coordinates, atomic and molecular integrals, configuration energies, and configuration interaction elements are available from the authors.

trices of the form

$$\begin{bmatrix} 0 & -\beta_{12} & -\beta_{13}\ldots\ldots\ldots-\beta_{1N} \\ -\beta_{21} & 0 & -\beta_{23}\ldots\ldots\ldots-\beta_{2N} \\ -\beta_{31} & -\beta_{32} & 0\ldots\ldots\ldots\ldots-\beta_{3N} \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ -\beta_{N1} & -\beta_{N2} & -\beta_{N3}\ldots\ldots\ldots 0 \end{bmatrix}$$

where β is the corresponding number in $\mathbf{H_{core}}$. For butadiene (II), α was calculated from eq. 18 with the Coulomb penetration integrals $(q:pp)$ evaluated according to Parr and Crawford[57] and $(r:pp)$ neglected; eq. 19 was used for the other compounds. The spectroscopic value of 11.080 e.v.[58] was used for the one-center two-electron Coulomb repulsion integral γ_{11}, and -11.22 e.v. for the ionization potential W_c.

(57) R. G. Parr and B. L. Crawford, Jr., *J. Chem. Phys.*, **16**, 1049 (1948). These integrals are evaluated using hydrogenic orbitals. Slater orbitals would be more consistent since they are used for the other integrals calculated, but the differences are small. Later calculations of the N → V₁ energy for *cis*- and *trans*-II, neglecting penetration integrals, including $(q:pp)$ for Slater orbitals with $(r:pp)$ zero, and including both $(q:pp)$ and $(r:pp)$, gave results constant to within 3 mμ for both isomers.

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

The Addition of Acylcobalt Carbonyls to Acetylenes. π-(2,4)-(Alkeno-4-lactonyl)cobalt Tricarbonyl Derivatives and Their Conversion to 2,4-Pentadieno-4-lactones

By Richard F. Heck

Acylcobalt tetracarbonyls react with substituted acetylenes to form π-(2,4)-(alkeno-4-lactonyl)cobalt tricarbonyl derivatives. These complexes react with triphenylphosphine, with evolution of carbon monoxide, to form mono(triphenylphosphine) derivatives. The acetylcobalt tetracarbonyl–3-hexyne–triphenylphosphine complex was isolated and characterized. Reactions of the π-lactonyl complexes were investigated. The most significant finding was a new method of synthesizing 2,4-pentadieno-4-lactones by the reaction of π-lactonyl complexes with dicyclohexylethylamine.

Introduction

Alkyl- and acylcobalt carbonyls react readily with many compounds having unshared electron pairs. Phosphines[1,2] and phosphites[3] form acylcobalt tricarbonyl monophosphines or monophosphites. The alkyl- and acylcobalt carbonyls can react with olefins to form ketones[4] and with conjugated dienes to form 1-acylmethyl-π-allylcobalt tricarbonyls.[5] The present paper is concerned with the reaction of acetylenes with acylcobalt carbonyls.

Many reactions of acetylenes with transition metal carbonyls and their derivatives are known, but there ap-

pear to be only a few examples of the reaction of alkyl- (or acyl)-metal carbonyls with acetylenes. Coffield reported that methylmanganese pentacarbonyl reacted with acetylene at 150° under pressure to produce π-dihydropentalenylmanganese tricarbonyl.[6] The fate of the methyl group was not determined. Zeiss has investigated the reactions of various aryl- and alkylchromium compounds and other transition metal alkyls with acetylenes and found that aromatic trimers are formed, sometimes accompanied by products containing two acetylene units and an alkyl[7] or aryl group from the metal.[8] Diethylnickel and diphenylacetylene yielded tetraphenylcyclohexadiene as well as hexa-

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