

C. *Nonalternant Hydrocarbons.* We have also carried out calculations by the method developed here for the nonalternant conjugated hydrocarbons listed in Figure 5. The resonance energies calculated by the Hückel, PPP, and SPO methods are listed in Table IX and the calculated bond lengths in Table X. Experimental values are also listed where these are available; the resonance energies were calculated from the observed stabilization energies by the method of Dewar and Schmeising.⁹ For comparison, calculated resonance energies for a selection of normal alternant aromatic hydrocarbons are shown in Table XI.

Table XI. Resonance Energies of Benzenoid Hydrocarbons

Molecule ^a	Formula	E_R , ^b e.v.		
		Hückel	PPP	SPO
Benzene (I)	C ₆ H ₆	1.318	1.318	1.318
Naphthalene (II)	C ₁₀ H ₈	2.413	2.282	2.280
Anthracene (III)	C ₁₄ H ₁₀	3.784	3.086	3.078
Phenanthrene (IV)	C ₁₄ H ₁₀	3.891	3.455	3.434
Pyrene (V)	C ₁₆ H ₁₀	4.254	4.008	3.973
Naphthacene (VI)	C ₁₈ H ₁₂	4.485	3.834	3.813
3,4-Benzphenanthrene (VII)	C ₁₈ H ₁₂	4.689	4.550	4.520
1,2-Benzanthracene (VIII)	C ₁₈ H ₁₂	4.639	4.329	4.307
Chrysene (IX)	C ₁₈ H ₁₂	4.711	4.553	4.512
Triphenylene (X)	C ₁₈ H ₁₂	4.777	4.792	4.730
Perylene (XI)	C ₂₀ H ₁₂	5.395	5.120	5.063

^a Geometries of these molecules will be found in Figure 1 of part I. ^b The values of $E_{\pi b}$ used to compute E_R were derived from molecular structures with equal bond lengths of 1.40 Å.

The resonance energies for the nonalternant hydrocarbons agree well in general with those of part I.

Once again the resonance energies are uniformly much less than for analogous alternant compounds, and once again the resonance energy for azulene is predicted to be much greater than for the other nonalternants. This is consistent with the experimental evidence, which suggests that azulene alone among these is aromatic.

The remaining nonalternants are, it is true, predicted to have positive resonance energies, but these are relatively small; since the compounds are all quite highly strained, and since this strain would be relieved by reactions in which one or more double bonds were destroyed, one might have expected such compounds to be highly reactive. The values listed in Table X moreover indicate that the bonds in most cases show strong alternation; such compounds would not then be classed as aromatic, being highly reactive and containing "localized" single and double bonds. This point is discussed further in the following paper.¹⁰

These arguments do not apply to pentalene and heptalene, where the circumferential bonds are predicted to be essentially equal in length. These compounds, though possibly highly reactive, should then show the characteristics typical of aromatic compounds (delocalization of π -electrons, ring current, etc.). While this conclusion could be avoided in the case of heptalene, where ring strain could favor a nonplanar geometry with consequent disruption of the π -systems, the prediction seems quite definite in the case of pentalene. It will be extremely interesting to see if pentalene does indeed turn out to be aromatic, though highly reactive; the available evidence certainly suggests that it is highly reactive, all attempts to prepare it having failed.

Ground States of Conjugated Molecules.

III. Classical Polyenes¹

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The SCF-LCAO-MO method described in previous^{2,3} papers of this series has been applied to a number of classical polyenes (i.e., polyenes for which only single unexcited resonance structures can be written). The results suggest that bond energies are additive in compounds of this type, it being possible to absorb the π -contributions to the "single" bonds into the empirical C-C bond energy. Compounds of this type are therefore "nonresonating" in the chemical sense of the term.

Introduction

For many years it was an accepted principle of chemical theory that the π -electrons in conjugated molecules

are delocalized, and that compounds of this type must, in valence bond terminology, be represented as resonance hybrids rather than by single classical structures. Recently this view has been questioned⁴ for the special case of classical conjugated molecules, such a molecule being one for which only a single classical (unexcited) resonance structure can be written. The purpose of this paper is to examine certain aspects of ideas which have been presented^{5,6} in this connection.

Much of the controversy over bond fixation and resonance has been based on misunderstandings of the fundamental issues involved. There is, in fact, no such thing as a localized bond; even in saturated molecules, such as paraffins, the valence electrons must, according

(1) This work was supported by the National Institutes of Health, U. S. Public Health Service, through Grant No. GM-11531-01.

(2) M. J. S. Dewar and A. L. H. Chung, *J. Chem. Phys.*, in press.

(3) M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.*, **87**, 685 (1965).

(4) See M. J. S. Dewar, "Hyperconjugation," Ronald Press Co., New York, N. Y., 1962.

(5) M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **5**, 166 (1959); **11**, 96 (1960).

(6) M. J. S. Dewar, *ibid.*, **19**, 89 (1963).

to current quantum theory, be completely delocalized. However, such a molecule may behave in certain respects *almost as if* the electrons in it were localized in definite bonds; in other words, certain properties of the molecule may have values closely similar to those calculated for such an artificial model. If so, the resulting "as if" picture provides a convenient and simple description; from a practical standpoint these advantages outweigh any theoretical deficiencies.

The success of the localized bond model can be explained^{4,6} in terms of simple MO theory. If we start with an artificial model for the molecule in which the valence electrons are localized in definite bonds, and if we then consider the effects of interactions between these localized bonds, we find that the interactions should have no first-order effect on the collective properties of the molecule, *i.e.*, properties which depend on all the electrons taken together (heat of formation, molecular geometry, dipole moment, etc.). If the original model was such that the interactions between bonds are small so that second-order effects can be neglected, the collective properties would then be well represented by the localized bond model. Such a situation should hold for a classical molecule where interactions between the localized bonds of its single classical structure should be small.

These arguments imply that bond fixation is a purely artificial concept, justified by its utility rather than its truth. This in turn implies that the sole criterion of bond fixation must be empirical; a molecule can be regarded as having localized bonds if its collective properties can be represented as additive functions of bond properties (bond energies, bond lengths, bond angles, bond dipole moments, etc.), with the proviso that the properties of a given bond may vary with the state of hybridization of the terminal atoms.⁵ "Resonance" in this chemical sense is then a measure of the extent to which the observed properties of the molecule differ from those calculated assuming additivity.

On this basis molecules may be representable in terms of localized bonds even if the second-order interactions between them are not negligible; for it may be possible to absorb a correction for these interactions into the empirical bond properties. For instance, classical polyenes might be representable in terms of localized single and double bonds even if there were "really" significant interactions between the latter; so long as the interactions between two adjacent double bonds are much the same in different molecules, they can be absorbed into the empirical bond properties for a C-C "single" bond between sp²-hybridized carbon atoms. The purpose of this paper is to examine the extent to which this type of compensation might be expected to hold.

Theoretical Method

If we make the usual Hückel approximation of treating σ - and π -electrons independently, the heat of formation (ΔH) of a conjugated hydrocarbon can be written in the form

$$\Delta H = E_{\sigma b} + E_{\pi b} \quad (1)$$

where $E_{\sigma b}$ and $E_{\pi b}$ are the σ - and π -binding energies, respectively. If we assume that the σ -bonds can be

represented as localized

$$E_{\sigma b} = \sum_{i,j} E_{\text{CH}}^{\sigma ij} + \sum_{k,l} E_{\text{CC}}^{\sigma kl} \quad (2)$$

where $E_{\text{CH}}^{\sigma ij}$ and $E_{\text{CC}}^{\sigma kl}$ are σ -bond energies for the bonds C_iH_j and C_kC_l , respectively. The π -binding energy can be expressed in the form

$$E_{\pi b} = E_{\pi} - nW_{2p} + E_{\text{cr}} \quad (3)$$

where E_{π} is the total energy of the n π -electrons, W_{2p} is the binding energy of a 2p-electron on an isolated carbon atom in its sp²-hybridized valence state, and E_{cr} is the total core repulsion energy. Previous papers of this series^{2,3} have described a modified Pople SCF-MO method for calculating these quantities and so estimating $E_{\pi b}$. The refined treatment of part II³ further permits bond lengths to be estimated as well as the total π -binding energy.

In the previous papers,^{2,3} this treatment was applied to a variety of aromatic and pseudoaromatic systems where the mean bond lengths are almost invariant; in this case the σ -binding energy can reasonably be written in the form

$$E_{\sigma b} = n_{\text{H}}E_{\text{CH}} + n_{\text{C}}E_{\text{CC}}^{1.40\text{\AA}} \quad (4)$$

where E_{CH} is the bond energy of a CH σ -bond formed by sp² carbon, while $E_{\text{CC}}^{1.40\text{\AA}}$ is the bond energy of the σ -component of an "aromatic" CC bond of length 1.40 Å. The heats of formation calculated in this way for a wide range of hydrocarbons seemed to agree with experiment. Our object here is to test the prediction⁵ that classical polyenes can be represented in terms of "localized" bonds. If so

$$\Delta H = n_{\text{H}}E_{\text{CH}} + n_{\text{C}}'E_{\text{CC}}' + n_{\text{C}}''E_{\text{CC}}'' \quad (5)$$

where n_{C}' is the number of CC "single" bonds of (empirical) bond energy E_{CC}' , while n_{C}'' and E_{CC}'' are the corresponding quantities for the CC "double" bonds. We can also write ΔH in the form

$$\Delta H = E_{\pi b} + n_{\text{C}}'E_{\text{CC}}^{\text{s}} + n_{\text{C}}''E_{\text{CC}}^{\text{d}} + n_{\text{H}}E_{\text{CH}} \quad (6)$$

where E_{CC}^{s} is the σ -bond energy of a "single" bond, E_{CC}^{d} that of a "double" bond, all "single" bonds having by assumption a common length, and likewise all double bonds.

Combining eq. 5 and 6

$$E_{\pi b} = n_{\text{C}}'(E_{\text{CC}}' - E_{\text{CC}}^{\text{s}}) + n_{\text{C}}''(E_{\text{CC}}'' - E_{\text{CC}}^{\text{d}}) \quad (7)$$

or

$$E_{\pi b} = n_{\text{C}}'E_{\pi}' + n_{\text{C}}''E_{\pi}'' \quad (8)$$

where E_{π}' and E_{π}'' are constants, being the π -energies of CC "single" and "double" bonds, respectively.

We can then test the correctness of our assumption that such molecules can be represented in terms of localized bonds by seeing whether the calculated values of $E_{\pi b}$ agree with eq. 8. If eq. 8 holds, then we can expect to represent the heats of formation of such molecules as additive functions of fixed properties of CC "single" and "double" bonds.

Results and Discussion

Calculations were first carried out for a series of open-chain polyenes (I), assuming an all-*trans* conformation in each case, with valence angles of 120°. Values for

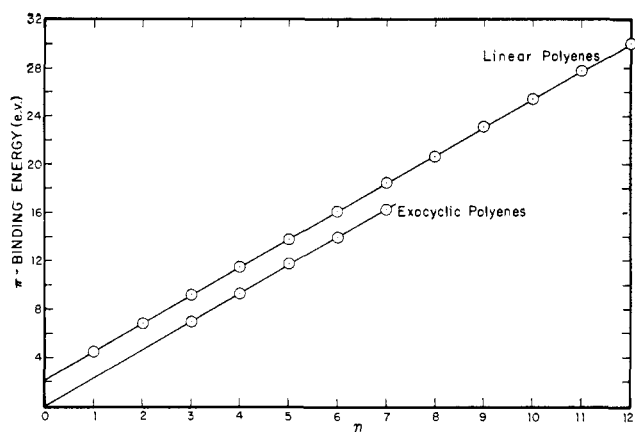
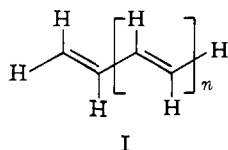


Figure 1. Plot of E_{π_b} vs. n for open-chain and exocyclic polyenes; values of E_{π_b} taken from the last column of Table I.

E_{π_b} were calculated by the PPP and SPO methods, following the procedure of part II³ and using values for integrals estimated by the methods described there. Calculations were carried out first for a model with all CC bonds equal in length (1.40 Å), and secondly for a



model made self-consistent for changes in integrals with bond length. Calculations for the first model were also carried out by the simple Hückel method. Table I shows the corresponding values for E_{π_b} , and

Table I. π -Binding Energies for Linear Conjugated Polyenes

n	E_{π_b} , e.v.				
	Hückel ^a	PPP ^a	SPO ^a	PPP ^b	SPO ^b
1	3.555	3.752	3.600	4.535	4.441
2	5.555	5.947	5.632	6.968	6.773
3	7.566	8.150	7.666	9.401	9.105
4	9.581	10.355	9.702	11.833	11.434
5	11.600	12.560	11.737	14.263	13.763
6	13.620	14.766	13.772	16.693	16.091
7	15.641	16.971	15.807	19.121	18.418
8	17.663	19.177	17.842	21.549	20.744
9	19.685	21.382	19.876	23.976	23.069
10	21.707	23.586	21.910	26.402	25.394
11	23.730	25.791	23.943	28.828	27.718
12	25.753	27.995	25.976	31.253	30.042

^a All bonds kept equal to 1.40 Å. ^b Bonds allowed to assume self-consistent values.

Table II lists bond lengths calculated by the method of part II by both the Pople and SPO methods; here n is the number of CC "single" bonds, the number of CC "double" bonds being $(n + 1)$.

If eq. 8 holds for these compounds

$$E_{\pi_b} = (n + 1)E_{\pi'} + nE_{\pi''} \\ = n(E_{\pi'} + E_{\pi''}) + E_{\pi'} \quad (9)$$

Thus a plot of E_{π_b} against n should be a straight line of slope $(E_{\pi'} + E_{\pi''})$ and intercept $E_{\pi'}$. The values for E_{π_b} listed in Table I follow this relation accurately; Figure 1 shows a typical plot using SPO results. From

Table II. Average Estimated Bond Lengths (Å)

n	PPP		SPO	
	Single bond	Double bond	Single bond	Double bond
1	1.461	1.344	1.468	1.342
2	1.458	1.346	1.466	1.344
3	1.457	1.348	1.465	1.345
4	1.456	1.349	1.465	1.345
5	1.456	1.350	1.464	1.346
6	1.455	1.350	1.464	1.346
7	1.455	1.351	1.464	1.346
8	1.455	1.351	1.464	1.347
9	1.454	1.351	1.463	1.347
10	1.454	1.351	1.463	1.347
11	1.454	1.352	1.463	1.347
12	1.454	1.352	1.463	1.347

Table III. Values for Components of the π -Binding Energies of Linear Conjugated Polyenes

	Hückel ^a	PPP ^a	SPO ^a	PPP ^b	SPO ^b
$E_{\pi'}$, e.v.	0.5052	0.6652	0.4702	0.3142	0.2047
$E_{\pi''}$, e.v.	1.5139	1.5394	1.5643	2.1146	2.1225

^a All bonds kept equal to 1.40 Å. ^b Bonds allowed to assume self-consistent values.

the slopes and intercepts values for $E_{\pi'}$ and $E_{\pi''}$ were determined; these are shown in Table III.

Several conclusions follow from these results.

(i) As one would expect, the polyenes are much more stable in configurations with alternating bond lengths than in symmetrical configurations with all bonds equal. The differences in total π -energy are very large. This clearly emphasizes the inadequacy of the simple Hückel method, with all resonance integrals set equal, for dealing with molecules of this type.

(ii) Table II shows that the calculated lengths of "single" bonds vary very little along the series (extreme values 1.454–1.461 Å. for PPP values, 1.463–1.466 Å. for SPO values), and that the same is also true for the "double" bonds (corresponding ranges 1.344–1.352 and 1.342–1.347 Å.). The use of a common value E_{CC} for the σ -energy of a "single" bond, and of a second common value E_{CC}^d for the σ -bond energy of a "double" bond, is therefore self-consistent. The linearity of the plot of E_{π_b} against n for the self-consistent values listed in the last two columns of Table I therefore shows that the heats of formation can be consistently expressed as additive functions of empirical bond energies (eq. 5).

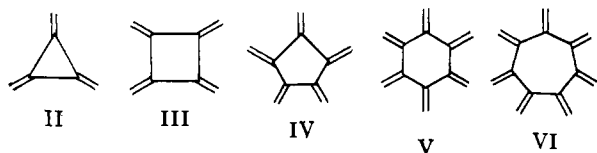
(iii) The π -bond energies for a CC "double" bond listed in the last two columns of Table III agree very closely with that calculated for ethylene, assuming bond length of 1.34 Å. (2.094 e.v.).

(iv) The estimated lengths for CC "single" bonds seem rather short; the central bond in butadiene is reported⁷ to have a length of 1.483 ± 0.001 Å. From this point of view the SPO method seems somewhat more satisfactory than the PPP method. The discrepancy is probably due to neglect of overlap in these Pople-type treatments; the bond order for the central bond in butadiene is reduced greatly by inclusion of

(7) A. Almennigen, O. Bastiansen, and M. Traettberg, *Acta Chem. Scand.*, 12, 1221 (1958).

overlap. A second factor is the inherent uncertainty in our method² for calculating bond lengths. However, the discrepancy is not large, and our main point, that the calculated lengths vary little from one compound to another, holds good in any case.

Having thus shown that eq. 8 should hold for the linear polyenes (I), the next step was to test it against classical polyenes of other types. We first studied the series of "exocyclic" polyenes, II-VI, these being assumed to be coplanar, the rings forming regular polygons. The corresponding values for $E_{\pi b}$, and for



the lengths of the "single" and "double" bonds, are shown in Table IV.

Table IV. Results for Exocyclic Polyenes

Compound	II	III	IV	V	VI
$E_{\pi b}$ (PPP), e.v.	7.286	9.715	12.144	14.573	16.963
(SPO), e.v.	6.982	9.309	11.636	13.963	16.290
Single bond length					
(PPP), Å.	1.463	1.464	1.460	1.460	1.459
(SPO), Å.	1.469	1.469	1.465	1.466	1.465
Double bond, length					
(PPP), Å.	1.349	1.348	1.350	1.350	1.351
(SPO), Å.	1.346	1.346	1.347	1.347	1.348

In these compounds the numbers of double and single bonds are equal ($= n$); hence eq. 8 becomes

$$E_{\pi b} = n(E_{\pi'} + E_{\pi''}) \quad (10)$$

A plot of $E_{\pi b}$ against n should therefore be a straight line, parallel to the corresponding plot for the linear polyenes but passing through the origin. This relation is obeyed accurately; Figure 1 shows the plot for the SPO results. Comparison of Tables II and IV also shows that the estimated lengths of "single" and "double" bonds agree closely; the exocyclic polyenes can therefore be well represented in terms of "localized" single and double bonds.

Calculations were also carried out for the branched chain polyenes VII-X. Table V compares values for $E_{\pi b}$ estimated directly with those found using the values

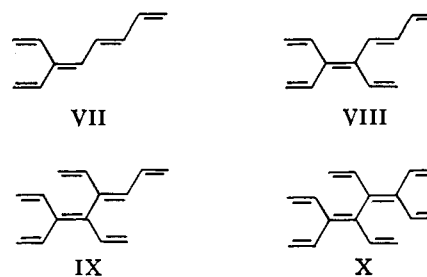
Table V. Comparison of Values for $E_{\pi b}$ for Branched Polyenes

Compound	$E_{\pi b}$, e.v. ^a			
	PPP		SPO	
	A	B	A	B
VII	11.831	11.830	11.435	11.432
VIII	14.313	14.259	13.800	13.759
IX	16.743	16.688	16.132	16.086
X	19.224	19.117	18.496	18.413

^a A, calculated directly; B, calculated from bond additivity.

for "localized" π -bond energies ($E_{\pi'}$ and $E_{\pi''}$) listed in Table III. The agreement is very good. The calculated bond lengths, listed on the formulas VII-X, also agree very closely with those found for the linear and exocyclic polyenes. Evidently the branched-chain

polyenes can also be well represented in terms of "localized" bonds.



These results indicate that if our method for calculating heats of formation of hydrocarbons is reliable, then the heats of formation of classical polyenes in general can be represented as additive functions of bond energies, and the bond lengths likewise vary very little from one compound to another. Since the results given in parts I² and II³ strongly support the trustworthiness of our method of calculation, these results therefore strongly support the contention⁵ that classical polyenes are nonresonating compounds, using the term in the empirical sense indicated above.

Resonance Energies

The expression for resonance energy given in part II³ was based on the assumption that all bonds are equal in length, an assumption which is not at all valid for compounds where there is a strong alternation in length between "single" and "double" bonds. Here one must use more general equation

$$E_R = \sum_{i,j} E_{CCij}^{\sigma} + E_{\pi b} - n_C' E_{CC'} - n_C'' E_{CC''} \quad (11)$$

which in the case of compounds with strong localization reduces to

$$E_R = n_C'(E_{CC^s} - E_{CC'}) + n_C''(E_{CC^d} - E_{CC''}) + E_{\pi b} \quad (12)$$

Table VI shows values for E_{CC^s} and E_{CC^d} , estimated for the indicated bond lengths, which are means of those given previously in this paper for "localized" single and double bonds. Table VII shows resonance

Table VI. σ -Energies for Carbon-Carbon (sp^2 - sp^2) Bonds

	PPP	SPO
Single bond length, Å.	1.456	1.464
E_{CC^s} , e.v.	3.8761	3.9926
Double bond length, Å.	1.350	1.345
E_{CC^d} , e.v.	3.6413	3.6361

energies calculated for the linear polyenes, using eq. 12 and the values listed in Table VI. The resonance energies are all close to zero, further supporting our contention that these compounds can be well represented, in the chemical sense, by the localized bond model.

These results suggest that the calculations of resonance energies given in part II³ for certain of the non-benzenoid hydrocarbons need re-examination; in the case of such cyclic but classical polyenes as fulvene, fulvalene, etc., our calculations indicated a strong alternation of bond lengths. In such cases it should prove to be a better approximation to use eq. 12,

Table VII. Resonance Energies of Linear Polyenes^a

<i>n</i>	<i>E_R</i> , e.v.	
	PPP	SPO
1	-0.031	-0.019
2	-0.046	-0.023
3	-0.060	-0.028
4	-0.076	-0.035
5	-0.094	-0.043
6	-0.112	-0.051
7	-0.132	-0.061
8	-0.151	-0.071
9	-0.172	-0.083
10	-0.194	-0.094
11	-0.216	-0.107
12	-0.239	-0.119

^a From eq. 12.

rather than the equation of part II which was derived on the assumption that all bonds have a common length (1.40 Å.). Table VIII shows resonance energies calculated on this basis for the compounds that were predicted in part II to show strong bond alternation; the values are all close to zero, indicating that these "classical" hydrocarbons are also well represented in terms of "localized" single and double bonds.

Summary and Conclusions

The results and arguments presented in this paper seem to provide strong support for the idea⁵ that classical conjugated hydrocarbons can be well repre-

Table VIII. Resonance Energies of Some Nonbenzenoid Hydrocarbons^a

Molecule	<i>E_R</i> ^b , e.v.	
	PPP	SPO
Fulvene	+0.003	+0.020
Heptafulvene	-0.044	-0.011
Fulvalene	+0.053	+0.083
Sesquifulvalene	-0.013	-0.020
Heptafulvalene	-0.028	0.000

^a From eq. 12. ^b Allowing for bond alternation.

sented in terms of "localized" single and double bonds. It should perhaps be emphasized again that this applies only to collective properties, and only in the sense that bond localization is regarded in the empirical way indicated earlier. If we are concerned with one-electron⁴ properties of molecules, or with purely theoretical discussions of the nature of binding in conjugated molecules, then the localized bond picture fails; but in these cases the picture is inapplicable to *any* molecules, saturated or unsaturated, conjugated or nonconjugated.

An immediate corollary follows. If "resonance" in the chemical sense is unimportant in classical conjugated polyenes, then it must certainly be unimportant in "hyperconjugated" molecules, for there can be little doubt that the interaction between the localized bonds of an idealized model must be less important in the latter case.

The Radiolysis of 1,4-Cyclohexadiene and 1,4-Cyclohexadiene-¹⁴CH₃I Mixtures¹

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Contribution from the Radiation Research Laboratories, Mellon Institute, Pittsburgh, Pennsylvania. Received October 17, 1964

The radiolysis of 1,4-cyclohexadiene was studied in order to provide information about the reactions of cyclohexadienyl radicals. The disproportionation of cyclohexadienyl radical, produced by radiolysis of 1,4-cyclohexadiene, yields 1,4-cyclohexadiene, 1,3-cyclohexadiene, and benzene in a ratio of 2.74:1.0:3.74. In scavenging experiments with small amounts of ¹⁴CH₃I (0.11 mole %) the two methylcyclohexadienes (I and II) are formed in a ratio of 1.6 ± 0.3. The mechanism of a chain isomerization to 1,3-cyclohexadiene, which is observed in the radiolysis of 1,4-cyclohexadiene-¹⁴CH₃I mixtures, is discussed.

In a previous publication² we have reported the formation of 1,3- and 1,4-cyclohexadiene in the radiolysis of liquid benzene in a ratio of 1:2.7. This ratio appears to be quite surprising in view of the relative electron spin densities for the *ortho* and *para* positions of the cyclohexadienyl radical of 2 × 0.35:0.5.³ The

reason for the unexpected behavior of the cyclohexadienyl radical could be that 1,3-cyclohexadiene is consumed by secondary reactions or that the disproportionation of the cyclohexadienyl radical is controlled by factors other than the electron spin density. In order to provide further insight into this problem we have studied the radiolysis of 1,4-cyclohexadiene, pure and in presence of small amounts (0.11 mole %) of ¹⁴CH₃I.

Experimental

The 1,4-cyclohexadiene (Columbia Chemical Co.) was purified just before use by the same technique of vapor phase chromatography as employed in the analysis. The sample (about 0.1 ml.) was then degassed by vacuum line techniques and sealed in a glass bulb. For the mixture experiments, the required amount of ¹⁴C-methyl iodide⁴ was added to the sample before it was sealed. The sealed sample was then

(1) Supported, in part, by the U. S. Atomic Energy Commission.
(2) M. K. Eberhardt, *J. Phys. Chem.*, **67**, 2856 (1963).

(3) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **38**, 773 (1963).

(4) R. H. Holroyd and G. W. Klein, *J. Phys. Chem.*, **69**, 194 (1965).