suggests that the emission process is localized in the carbonyl moiety. This explanation is consistent with molecular orbital theory, since none of the compounds studied shows conjugation with the carbonyl group. It is well known that aromatic ketones, such as acetophenone and benzophenone, do not fluoresce.[1]

From the data in Tables I and II it is seen that the natural radiative lifetimes for singlet, $\tau_F{}^0 = 1/k_F$, and triplet, $\tau_p{}^0 = \tau_p\,\phi_T/\phi_p$, are relatively constant. The slight increase for $k_F$ with substitution is probably related to small variations of $\epsilon_{max}$. Since the triplet yields of the ketones, on the basis of available evidence,[12,17,20,23] can be assumed to be 1.00 ± 0.10, the intersystem crossing rates are expected to be approximately 90–100 times faster than the radiative singlet–singlet transition, *e.g.*, $k_{isc} \approx 100k_F$, assuming $k_{ds}$ is negligible. This condition is not true, however, when internal conversion of the singlet occurs. It is tempting to suggest that possibly the singlet and triplet manifold are affected in the same manner by alkyl substitution, *i.e.*, alkyl substitution at the $\alpha$ carbon in acetone slows down radiationless deactivation. Preliminary evidence indicates that the fluorescence yield of di-*t*-butyl ketone is greater than that for acetone.[24] A consequence of this interpretation is that there is a small amount of singlet deactivation in acetone ($\phi_{ds} \sim 0.03$), which is increasingly removed by modifying the molecule by alkyl substitution. The results for the phosphorescence in Table I confirm this effect in the triplet manifold.

In view of the above results, it is tempting to explain the increasing quantum yields associated with alkyl substitution in terms of the energies of the vibrational quanta of the C–H stretch (2900–3000 cm$^{-1}$), the C–D stretch ($\sim$2200 cm$^{-1}$), and the C–C stretch (600–1500 cm$^{-1}$).[25] In acetone, energy dissipation can occur *via* the C–H stretch. Since the C–C stretch involves a smaller quantum of energy than the C–H stretch, it is reasonable to expect that the probability of radiative emission would be increased upon systematic replacement of the $\alpha$ hydrogens with alkyl groups. The phosphorescence data for the series of ketones in Table I are consistent with this interpretation. Our observations of a deuterium effect on the emission properties with acetone-$d_6$ (see Table I) further corroborate this interpretation.

[24] M. O'Sullivan and A. C. Testa, unpublished work.

[25] R. T. Conley, "Infrared Spectroscopy," Allyn and Bacon, Inc., Boston, Mass., 1966, pp 92–93, 96.

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# Studies of Conjugated Ring Hydrocarbons: the Structure of Dimethylfulvene

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*Received May 28, 1969*

**Abstract:** Dimethylfulvene is one of a group of nonbenzoid conjugated ring hydrocarbons under investigation in this laboratory by electron diffraction. The intensity patterns produced by $C_5H_4CMe_2$ vapor were analyzed on the basis of a model with $C_{2v}$ symmetry, wherein a range of bond lengths and angles was tested in a variety of plausible combinations. A least-squares analysis was applied to the experimental molecular intensity curve, and this led to the following geometrical parameters: $C_1—C_2 = 1.476 \pm 0.008$, $C_2═C_3 = 1.340 \pm 0.006$, $C_3—C_4 = 1.462 \pm 0.009$, $C_1═C_6 = 1.347 \pm 0.010$, $C_6—C_7 = 1.510 \pm 0.010$, and $(C—H)_{av} = 1.100 \pm 0.010$ Å; $\angle C_4C_3C_2 = 109.0 \pm 1.2$, $\angle C_1C_6C_7 = 122 \pm 2$, $\angle C_4C_3H_{10} = 131 \pm 2$, and $\angle C_6C_7H = 108 \pm 2°$. The methyl groups have $C_{3v}$ symmetry with reference to the $C_7$–$C_6$ axis, apparently in a slightly distorted eclipsed conformation. Planar carbon skeleton models with uncoupled free rotation of the methyl groups and with staggered conformations were tested. None of these fit the reduced experimental molecular intensity curve better than the model with the methyl groups eclipsed.

Because fulvene is one of the isomers of benzene with three conjugated double bonds, its chemical and physical properties have been scrutinized for evidence of aromatic character. In this regard, a precision determination of its molecular geometry would probably support the chemical evidence that bonding in the fulvene framework is best described as a superposition of three butadiene-type structures. An early electron diffraction study[2] is not sufficiently conclusive, nor is the microwave analysis[3] of a single isotopic species, although the latter does prove that the molecule is planar. In the following report on the structure of dimethylfulvene the coplanarity of the carbon skeleton is again confirmed, as is the similarity of its interatomic distances to those present in butadiene. A comprehensive review of the chemistry of the fulvenes has been published recently;[4] less current are spectroscopic studies in the uv[5a] and ir[5b] and dipole moment calculations.[6]

## Experimental Section

The dimethylfulvene used in this investigation was prepared by Mr. H. Banks of the Department of Chemistry, Cornell University,

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[1] (a) State University College; (b) Cornell University.

[2] M. Rouault and Z. L. Waziutynska, *Acta Cryst.*, **10**, 804 (1957).

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

[4] E. D. Bergmann, *Chem. Rev.*, **68**, 41 (1968).

[5] (a) J. H. Day and J. C. Lukman, *Ohio J. Sci.*, **52**, 335 (1952); (b) J. C. Wood, R. M. Elofson, and D. M. Saunders, *Anal. Chem.*, **30**, 1339 (1958).

[6] G. W. Wheland and D. E. Mann, *J. Chem. Phys.*, **17**, 264 (1949).

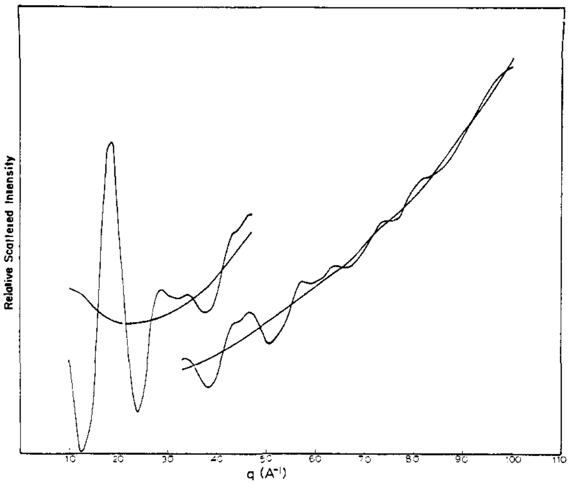

Figure 1. The experimental relative intensity and the "refined" background, for dimethylfulvene.

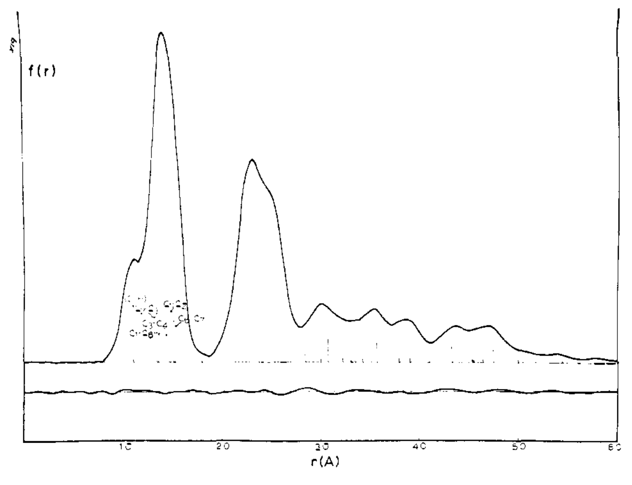

Figure 3. Radial distribution curve for dimethylfulvene. The lower oscillating curve is the difference between the experimental and theoretical radial distribution functions.

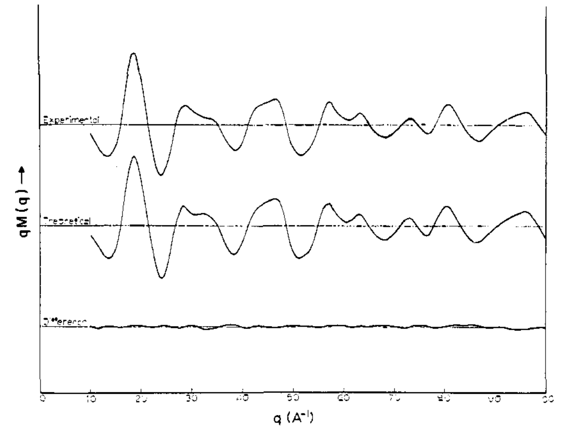

Figure 2. The reduced experimental molecular intensity curve for dimethylfulvene compared with that calculated for the best model. The lower oscillating curve is the difference between them.

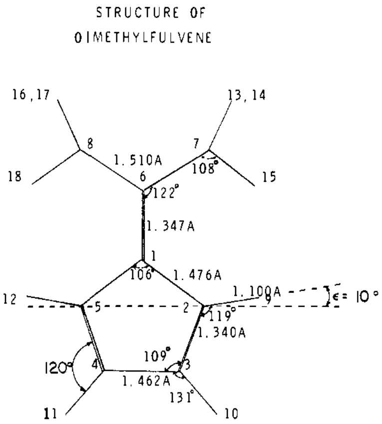

Figure 4. The structure of dimethylfulvene

according to the procedure of Smith, *et al.*[7] The product was purified by triple distillation and checked by vpc. The sample (bp 118–119°) was kept frozen in liquid nitrogen during storage. Sectored electron diffraction patterns were taken with the apparatus described previously,[8] using a 70-kV electron beam at two sample-to-plate distances (262 and 129 mm). To obtain sufficient vapor pressure for the electron diffraction photographs the temperature of the sample was raised to 0°. Magnesium oxide diffraction patterns were recorded concurrently to establish the scale factors. The patterns were photometered with a modified double beam Jarrell-Ash microdensitometer,[9] and the digitzed data were converted to intensities at unit intervals of $q$ $(40/\lambda \sin \theta/2)$, according to the procedures previously described.[10]

## Analysis and Results

The total experimental intensity curves for the two sets of data and the superposed "refined" background are shown in Figure 1. (These values are tabulated in the Appendix.) The reduced molecular intensity curve and a theoretical curve calculated for the best model as derived from the least-squares analysis are shown in Figure 2; the difference curve is also plotted. The radial distribution curve based on the refined background and the difference between that and the curve calculated for the best model are shown in Figure 3. All models used had $C_{2v}$ symmetry, but a wide range of bond lengths and angles, in plausible combinations, was tested in the analysis. The structural models were specified in terms of the following 12 geometrical parameters (refer to Figure 4): $C_1—C_2$, $C_2═C_3$, $C_3—C_4$, $C_1═C_6$, $C_6—C_7$, $(C—H)_{\text{vinyl}}$, $(C—H)_{\text{methyl}}$, $\angle C_2C_3C_4$, $\angle C_1C_6C_7$, $\angle C_4C_3H_{10}$, $\angle C_6C_7H_{13}$, and $\epsilon$, the angle between $C_2$–$H_9$ and the $x$ axis (on line with $C_2 \cdots C_5$). Models with uncoupled free rotation of the methyl groups and staggered conformation were also tested. None of these fit the experimental intensity and radial distribution functions better than the $C_{2v}$ model with the two methyl groups in eclipsed form, in which one of the methyl hydrogens is in the C-atom plane while the other two hydrogens are located above and below that plane.

A least-squares successive approximation calculation was applied to the reduced experimental molecular intensity function. The program converged after 12 cycles of iteration. In this analysis the following geometric parameters and mean square amplitudes of vibrations were allowed to vary: $C_1—C_2$, $C_2═C_3$, $C_3—C_4$, $C_1═C_6$, $C_6—C_7$, $\angle C_2C_3C_4$, $\angle C_1C_6C_7$, $l_{13}$, $l_{34}$, and $l_{12}$.

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[7] W. B. Smith and C. Gonzalez, *J. Org. Chem.*, **28**, 3541 (1963).

[8] S. H. Bauer and K. Kimura, *J. Phys. Soc. Jap.*, **17**, 300 (1962); S. H. Bauer, "Electron Diffraction at High Temperatures," Nonr-40(41), Project NR 092-504, ARPA Order No. 23-53.

[9] S. H. Bauer, R. Jenkins, and R. Hilderbrandt, submitted for publication.

[10] J. L. Hencher and S. H. Bauer, *J. Am. Chem. Soc.*, **89**, 5527 (1967).

The other $l_{ij}$'s were constrained to reasonable values. The set of parameters and $l_{ij}$'s which gave the lowest residuals and errors in the least-squares analysis are listed in Table I. The error matrix, reproduced in Table II, shows the extent of the correlations between $\angle C_2C_3C_4$ and the ring dimensions; also between $\angle C_1C_6C_7$ and the terminal dimensions; these are uncomfortably large, but inescapable in this molecule.

**Table I.** Structural Parameters for Dimethylfulvene

| Type | $r_{ij}$, Å or ∠, deg | $l_{ij}$, Å |
|---|---|---|
| $C_1—C_2$ | 1.476 ± 0.008 | 0.058 ± 0.004 |
| $C_2=C_6$ | 1.347 ± 0.010 | 0.043[a] |
| $C_2=C_3$ | 1.340 ± 0.006 | 0.043[a] |
| $C_3—C_4$ | 1.462 ± 0.009 | 0.058 ± 0.004 |
| $C_6—C_7$ | 1.510 ± 0.010 | 0.060[a] |
| $\langle C—H \rangle_{av}$ | 1.100 ± 0.010 | 0.084[a] |
| $\angle C_4C_3C_2$ | 109.0 ± 1.2 | |
| $\angle C_1C_6C_7$ | 122.0 ± 2.0 | |
| $\epsilon$[b] | 10.0 | |
| $\angle C_4C_3H_{10}$ | 131.0 ± 2.0 | |
| $\angle C_6H_7H$ | 108 ± 2.0 | |
| $\angle C_1C_2C_3$ | (108) | |

[a] Assumed value and constrained during the least squares analysis. [b] For definition, see Figure 4.

**Table II.** Error Matrix of Dimethylfulvene

| | $C_1—C_2$ | $C_2=C_3$ | $C_3—C_4$ | $C_1=C_6$ | $C_6=C_7$ | $\angle C_2C_3C_4$ | $\angle C_1C_6C_7$ | $l_{13}$ | $l_{34}$ | $l_{12}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $C_1—C_2$ | 0.0026 | | | | | | | | | |
| $C_2=C_3$ | 0.0017 | 0.0020 | | | | | | | | |
| $C_3—C_4$ | −0.0011 | −0.0019 | 0.0028 | | | | | | | |
| $C_1=C_8$ | 0.0020 | 0.0030 | −0.0001 | 0.0033 | | | | | | |
| $C_6$--$C_7$ | 0.0019 | 0.0002 | 0.0005 | 0.0040 | 0.0034 | | | | | |
| $\angle C_2C_3C_4$ | −0.1250 | 0.1751 | −0.2512 | −0.0112 | 0.1507 | 0.4021 | | | | |
| $\angle C_1C_6C_7$ | −0.0850 | −0.1620 | −0.0126 | 0.4130 | 0.3844 | 0.5112 | 0.6590 | | | |
| $l_{13}$ | 0.0007 | 0.0030 | 0.0029 | −0.0021 | −0.0027 | −0.0720 | 0.0010 | 0.0010 | | |
| $l_{34}$ | 0.0009 | −0.0013 | 0.0012 | −0.0057 | 0.0091 | 0.0089 | 0.0092 | −0.0025 | 0.0012 | |
| $l_{12}$ | −0.0011 | −0.0025 | 0.0081 | 0.0033 | 0.0078 | −0.0051 | −0.0037 | 0.0007 | 0.0002 | 0.0013 |

Figure 5 shows the second peak of the radial distribution function on an expanded scale. This peak is mainly due to the nonbonded C···C and C···H distances. It is well reproduced by assigning $C_1 \cdots C_3$ = 2.273, $C_2 \cdots C_4$ = 2.289, $C_2 \cdots C_5$ = 2.356, $C_1 \cdots C_7$ = 2.500, $C_2 \cdots C_6$ = 2.527, $C_7 \cdots C_8$ = 2.561, $C_3 \cdots H_9$ = 2.103, $C_2 \cdots H_{10}$ = 2.108, $C_6 \cdots H_{13}$ = 2.171, $C_3 \cdots H_{11}$ = 2.323, $C_1 \cdots H_9$ = 2.358, $C_2 \cdots H_{15}$ = 2.566, and $C_1 \cdots H_{15}$ = 2.624 Å. These are indicated by vertical lines along the abscissa, with their heights proportional to the quantity, $n_{ij}Z_iZ_j/r_{ij}$, where $n_{ij}$ is the number of atom pairs at the distance $r_{ij}$, with atomic numbers $Z_i$ and $Z_j$. The locations of the other bonded and nonbonded distances are shown in Figure 3.

## Discussion

The coplanarity of the carbon skeleton in dimethylfulvene has been confirmed in this investigation, in view of the small amplitudes of the difference curves in Figures 2 and 3. The ring skeleton dimensions are in good agreement with those reported for cyclopentadiene,[11] except for the anticipated difference in the length of $C_1$–$C_2$. The comparison is presented in Table III.

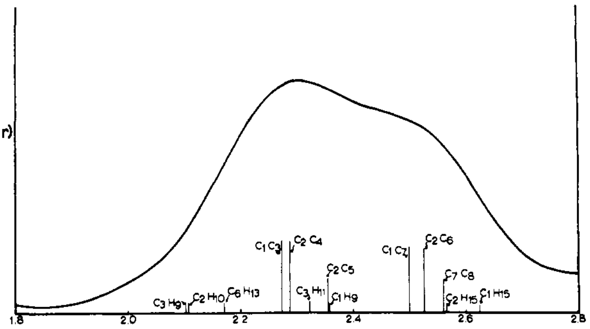

Figure 5. An expanded view of the 1.8–2.8 Å region of Figure 3.

The moments of inertia and rotational constants of fulvene were calculated using the skeletal dimensions derived in this study for dimethylfulvene. The calculated rotational constants were then compared with those reported in the microwave study[3] as listed in Table IV. The agreement suggests (but does not prove) that methyl substitution has no significant effect on the skeletal dimensions. Of course, such an indirect check of geometric parameters as derived from microwave and electron diffraction techniques is gratifying. The error limits listed in Table I are approximately three

**Table III.** Comparison of Skeletal Dimensions in Dimethylfulvene and Cyclopentadiene

| | Dimethylfulvene | Cyclopentadiene[a] |
|---|---|---|
| $C_1—C_2$, Å | 1.476 | 1.509 |
| $C_2=C_3$, Å | 1.340 | 1.342 |
| $C_3—C_4$, Å | 1.462 | 1.469 |
| $\angle C_2C_3C_4$, deg | 109.0 | 109.4 |
| $\angle C_2C_1C_5$, deg | 107 | 102.8 |

[a] Reference 11.

**Table IV.** Moments of Inertia and Rotational Constants of Fulvene and Dimethylfulvene

| | Fulvene, calcd | Fulvene, MW[a] | Dimethylfulvene, calcd |
|---|---|---|---|
| $I_z$, g cm$^2$ | $1.0248 \times 10^{-38}$ | | $1.994 \times 10^{-38}$ |
| $I_x$, g cm$^2$ | $2.1977 \times 10^{-38}$ | | $5.379 \times 10^{-38}$ |
| $I_y$, g cm$^2$ | $3.2259 \times 10^{-38}$ | | $7.273 \times 10^{-38}$ |
| $A_{(z)}$, MHz | 8187.1 | 8189.505 | 7029 |
| $B_{(x)}$, MHz | 3817.1 | 3802.781 | 1560 |
| $C_{(y)}$, MHz | 2603.5 | 2596.449 | 1154 |

[a] Reference 3.

(11) L. H. Scharpen and V. W. Laurie, *J. Chem. Phys.*, **43**, 2765 (1965).

**Table V.** A Comparison of the Single and Double Bonds in Dimethylfulvene and Related Compounds

| | C=C | =C—C= | =C—CH$_2$ | Method (ref) |
|---|---|---|---|---|
| Ethylene | 1.3369 (0.001) | | | ED (12) |
| Propene | 1.336 | | 1.501 | MW (13) |
| Butadiene | 1.341 (0.002) | 1.463 (0.003) | | ED (14) |
| 2,3-Dimethylbutadiene | 1.349 | 1.491 | 1.511 | ED (15) |
| Cyclopentadiene | 1.342 | 1.469 | | MW (11) |
| Cyclohexadiene | 1.350 | 1.468 | | ED (16) |
| Cycloheptadiene | 1.350 | 1.480 | | ED (17) |
| 1,3,5-*trans*-Hexatriene | 1.337 (0.002) (terminal) | 1.458 (0.002) | | ED (18) |
| | 1.368 (0.004) (central) | | | |
| 1,3,5-*cis*-Hexatriene | 1.336 (terminal) | 1.462 | | ED (19) |
| | 1.362 (central) | | | |
| Cycloheptatriene | 1.356 | 1.446 | | ED (20) |
| Fulvene | 1.355 (ring) | 1.467 | | Calcd$^a$ |
| | 1.353 (side) | 1.456 | | |
| | 1.358 (ring) | 1.440 (base) | | Calcd$^b$ |
| | 1.356 (side) | 1.452 | | |
| Dimethylfulvene | 1.342 (av) | 1.471 (av) | 1.510 | ED (this study) |
| Dimethylenecyclobutene | 1.357 (ring) | 1.488 (C$_1$–C$_2$) | | ED (22) |
| | 1.335 (side) | 1.516 (C$_2$–C$_3$) | | |
| | 1.360 (ring) | 1.460 (C$_1$–C$_2$) | | Calcd$^b$ |
| | 1.345 (side) | 1.474 (C$_2$–C$_3$) | | |
| Trimethylenecyclopropane | 1.343 (0.020) | 1.453 (0.02) | | ED (23) |
| | 1.351 | 1.460 | | Calcd$^b$ |

$^a$ SCF MO LCAO calculation (ref 21). $^b$ Refined ω technique: E. A. Dorko, H. P. Nielsen, and W. C. Bahr, AFIT, private communication.

times the corresponding standard deviations; as such they exceed the estimated magnitudes of experimental errors arising from imprecision in the λ-L calibration, etc.

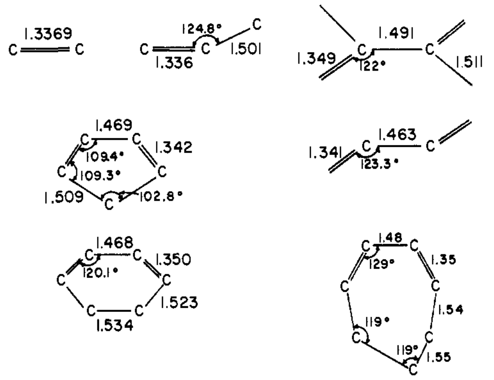

Figure 6. Comparison of distances and bond angles in various butadiene configurations.

One interesting feature of this structure is the angle which the C$_3$–H$_{10}$ bond makes with C$_2$–C$_3$ (and corresponding angles for C$_2$–H$_9$, etc). This has been noted for other cyclic olefins. Apparently, adjustment to the required internal angle by the C–C directed lobe of the sp$^2$ bond has no appreciable effect on the direction of the lobe directed toward the hydrogen atom which remains at the theoretical angle.

Imagine the building up of conjugated systems, by starting with ethylene, and substituting onto it a succession of methylene groups. The double bond length in ethylene is 1.337 Å[12] while in propene it is 1.336 Å.[13] Here the sp$^2$–sp$^3$ single bond is 1.501 Å. These dimensions provide reference values. In butadiene, the single bond is somewhat shorter, being 1.463 Å, as expected for sp$^2$–sp$^2$, while the double bond is the same or possibly slightly longer, 1.341 Å.[14] This is also the case in cyclopentadiene, but in cyclohexadiene and -heptadiene the double bond is ≈0.1 Å longer. Also, in the C$_7$ compound, the =C—C= bonds appear to be somewhat longer, possibly due to angle strain and nonbonded repulsions (refer to Figure 6 and Table V).[11–23] Consider now the conjugated trienes. As shown in Figure 7, the single and double bonds in a strainless (angle) 1,3,5-*trans*-hexatriene are 1.337 and 1.458 Å, respectively.[18,19] Ring closure to cycloheptatriene[20] leads to a somewhat expanded double bond length but somewhat shorter =C—C= lengths, roughly parallel to the observed dimensional differences between butadiene and cyclopentadiene.

The interesting questions arise when one imagines ring closure of hexatriene accompanied by loss of H$_2$, to form the various isomers of benzene: fulvene, dimethylenecyclobutene, and trimethylenecyclopropane. The classification of these as nonaromatics is based on extensive investigations of their chemical properties. As for structural criteria, it is evident by inspection that alternation of their carbon–carbon bond lengths is quantitatively best described as a superposition of butadiene-type structures; there is no resemblance to bond lengths characteristic of an aromatic molecule. As a consequence, one should anticipate variations in bond

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(12) L. S. Bartell, A. Roth, C. D. Hollowell, K. Kuchitsu, and J. E. Young, *J. Chem. Phys.*, **42**, 2683 (1965).

(13) D. R. Lide, Jr., and D. Christensen, *ibid.*, **35**, 1374 (1961).

(14) K. Kuchitsu, T. Fukuyama, and Y. Morino, *J. Mol. Struct.*, **1**, 463 (1968).

(15) C. F. Aten, L. Hedberg, and K. Hedberg, *J. Am. Chem. Soc.*, **90**, 2463 (1968).

(16) H. Oberhammer and S. H. Bauer, *ibid.*, **91**, 11 (1969).

(17) J. F. Chiang and S. H. Bauer, *ibid.*, **88**, 420 (1966).

(18) M. Traetteberg, *Acta Chem. Scand.*, **22**, 628 (1968).

(19) M. Traetteberg, *ibid.*, **22**, 2294 (1968).

(20) M. Traetteberg, *J. Am. Chem. Soc.*, **86**, 4265 (1964).

(21) A. Skancke and P. N. Skancke, *Acta Chem. Scand.*, **22**, 175 (1968).

(22) A. Skancke, private communication.

(23) E. A. Dorko, J. L. Hencher, and S. H. Bauer, *Tetrahedron*, **24**, 2425 (1968).

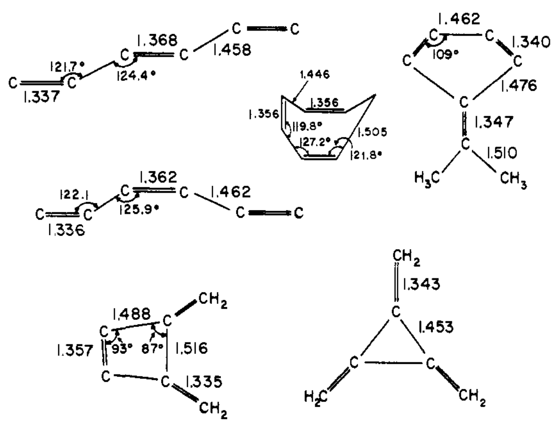

Figure 7. Comparison of distances and bond angles in conjugated trienes.

lengths (at the ±0.01 Å level), depending in detail on their conformations, due to differences in nonbonded repulsions and angle strain. In contrast, such variations are not observed in truly aromatic systems, wherein the replacement of a hydrogen atom by a wide range of substituents has little or no effect on the dimensions of the carbon skeleton.[24]

An explanation for the dramatic difference in the relative stabilization due to delocalization of the $\pi$ electrons between benzene and these isomers is not easily verbalized. The calculated heats of formation are surprisingly close to those observed.[25] In a recent review, Jones[26] discussed various criteria that have been proposed for aromatic character. The bond distance criterion as accepted in the present discussion is clearly the most reliable one. In our opinion, the molecule which merits the most careful analysis is trimethylenecyclopropane; it clearly has very little resonance stabilization.[23] One would have expected it to have more than the other two isomers in view of the electron delocalization inherent in cyclopropane rings, particularly according to the Walsh model.[27]

**Acknowledgments.** The authors wish to thank Messrs. L. Ma and R. Devine of the Computer Center, State University College at Oneonta, N. Y., and Messrs. J. Higgins and R. Roberson, Computer Center of the State University of New York at Binghamton, for the various help during the course of this analysis. Sincere thanks are due to Mr. H. Banks for preparing the sample of dimethylfulvene, and to Professor C. F. Wilcox, Jr. and Dr. W. B. Dixon for helpful discussions. This work was supported in part by a grant from the Material Science Center, Cornell University, Ithaca, N. Y.

## Appendix

| Set 1 | | Set 2 | | | |
|---|---|---|---|---|---|
| *q* | Intensity | *q* | Intensity | *q* | Intensity |
| 10 | 1.3753 | 33 | 0.7915 | 67 | 0.9781 |
| 11 | 1.1854 | 34 | 0.7927 | 68 | 0.9870 |
| 12 | 1.0238 | 35 | 0.7857 | 69 | 1.0002 |
| 13 | 1.0223 | 36 | 0.7650 | 70 | 1.0160 |
| 14 | 1.0939 | 37 | 0.7400 | 71 | 1.0320 |
| 15 | 1.2603 | 38 | 0.7360 | 72 | 1.0500 |
| 16 | 1.5585 | 39 | 0.7400 | 73 | 1.0650 |
| 17 | 1.9681 | 40 | 0.7000 | 74 | 1.0711 |
| 18 | 2.2372 | 41 | 0.7930 | 75 | 1.0709 |
| 19 | 2.2475 | 42 | 0.8341 | 76 | 1.0730 |
| 20 | 1.9761 | 43 | 0.8588 | 77 | 1.0792 |
| 21 | 1.6716 | 44 | 0.8650 | 78 | 1.0987 |
| 22 | 1.4170 | 45 | 0.8691 | 79 | 1.1208 |
| 23 | 1.2305 | 46 | 0.8819 | 80 | 1.1401 |
| 24 | 1.1701 | 47 | 0.8861 | 81 | 1.1510 |
| 25 | 1.2432 | 48 | 0.8760 | 82 | 1.1593 |
| 26 | 1.3875 | 49 | 0.8495 | 83 | 1.1608 |
| 27 | 1.5634 | 50 | 0.8265 | 84 | 1.1681 |
| 28 | 1.6434 | 51 | 0.8250 | 85 | 1.1730 |
| 29 | 1.6618 | 52 | 0.8340 | 86 | 1.1840 |
| 30 | 1.6460 | 53 | 0.8470 | 87 | 1.1920 |
| 31 | 1.6360 | 54 | 0.8660 | 88 | 1.2101 |
| 32 | 1.6298 | 55 | 0.8951 | 89 | 1.2260 |
| 33 | 1.6335 | 56 | 0.9285 | 90 | 1.2450 |
| 34 | 1.6442 | 57 | 0.9476 | 91 | 1.2636 |
| 35 | 1.6340 | 58 | 0.9458 | 92 | 1.2800 |
| 36 | 1.6031 | 59 | 0.9452 | 93 | 1.2978 |
| 37 | 1.5780 | 60 | 0.9470 | 94 | 1.3150 |
| 38 | 1.5750 | 61 | 0.9530 | 95 | 1.3320 |
| 39 | 1.5900 | 62 | 0.9620 | 96 | 1.3490 |
| 40 | 1.6436 | 63 | 0.9763 | 97 | 1.3618 |
| 41 | 1.7270 | 64 | 0.9802 | 98 | 1.3705 |
| 42 | 1.8200 | 65 | 0.9768 | 99 | 1.3785 |
| 43 | 1.8840 | 66 | 0.9759 | 100 | 1.3844 |
| 44 | 1.8977 | | | | |
| 45 | 1.9215 | | | | |
| 46 | 1.9580 | | | | |
| 47 | 1.9698 | | | | |

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