The Molecular Structure of Gaseous 2,3-Dimethylbutadiene[1]

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Abstract: The molecular structure of 2,3-dimethylbutadiene has been investigated by electron diffraction from the vapor. The molecule exists in the *trans* configuration and there is no evidence of deviation from heavy-atom coplanarity. Assuming molecular symmetry C_{2h} and symmetric C–CH_3 and C═CH_2 groups, the important distance, angle, and root-mean-square amplitude values were found to be C═C = 1.349 Å (0.006), C—C_{av} = 1.504 Å (0.005), C–H_{av} = 1.111 Å (0.014), $\angle C_1{=}C_2{-}C_3$ = 122.0° (2.0), ∠C—C—C = 117.9° (1.5), $l_{C=C}$ = 0.0407 Å (0.006), $l_{C_2-C_3}$ = 0.0448 Å (assumed), and $l_{C_2-C_5}$ = 0.0433 Å (0.007); parenthesized values are 2σ. The structure is not unusual, but the conjugated carbon–carbon single bond appears to be longer than that in butadiene by a significant amount.

The structures of organic molecules with sequences of alternating double and single bonds are especially important because of a widespread interest in the nature of the bonding in them. For example, there has been considerable discussion about the relative extent to which conjugation and hybridization effects contribute to the well-known shortening of single bonds adjacent to double bonds,[3] and it has even been possible to correlate bond lengths in terms of nonbond repulsive interactions without invoking either.[4] Despite this interest, however, accurate values for bond lengths in such systems are few,[5] and additional data are needed. The investigation reported here is one of a series on simple molecules which, it is hoped, will help to clarify some of the theoretical questions.

Experimental and Data Reduction

The 2,3-dimethylbutadiene was a redistilled commercial sample of >99% purity kindly provided by Professor W. von E. Doering and was used without further purification. Diffraction photographs were made in the Oslo apparatus[6] at camera distances of 48.032 and 19.332 cm with electrons of wavelength 0.06469 Å (as determined in separate diffraction experiments from gold foil) using an r^3 rotating sector. Four plates from each distance were selected for analysis and the data reduced in essentially the manner described earlier.[7] Two forms of intensity curve, I_m' and sI_m,[7] were used for the structure analysis. The first of these is shown in Figure 1, and, ignoring phase shift factors, corresponds to the equation[8]

$$I_m' = \sum_{i,j} r_{i,j}^{-1}(Z-f)_i(Z-f)_j(Z_C)^2(Z-f)_C^{-2} \times \exp(-l_{i,j}^2 s^2/2)\sin r_{i,j}s \qquad (1)$$

The quantities $(Z-f)_C$ were obtained from the tables of Hansen, *et al.*[9] The experimental intensity data covered the range $1.25 \leqslant s \leqslant 44.75$ at intervals $\Delta s = 0.25$.

Structure Analysis

The structure analysis followed standard procedure. Radial distribution curves were calculated from the intensity curve according to the equation

$$P(r)/r = \sum_{s=0}^{s_{max}} I_m'(s)\exp(-Bs^2)\sin rs \qquad (2)$$

These curves provided approximate values for the structural parameters of the molecule, which were close enough to the final values to be refined by least squares. Theoretical radial distribution curves and intensity curves were calculated at intervals throughout the analysis to provide evidence of its progress and, finally, to provide display of the quality of the agreement.

Experimental Radial Distribution Curve. The experimental curve shown in Figure 2 was calculated from the experimental intensity curve of Figure 1 according to eq 2 using the summation interval $\Delta s = 0.25$ over the range $0 \leqslant s \leqslant 44.75$. Data in the experimentally unobservable range $0 \leqslant s \leqslant 1.25$ were taken from a theoretical curve (calculated in the course of the analysis) for a model close to the final model. The value $B = 0.001$ was used for the curve shown: this value is large enough to prevent gross Fourier series termination errors but not so large as to seriously diminish the resolution of immediately adjacent peaks.

The experimental curve may be discussed in part by comparison with the theoretical curve also shown in Figure 2. The differences between these curves are, first, the (frequently encountered) weak maxima below 1.0 Å in the experimental curve due to unimportant low-frequency background errors and, second, the small, higher frequency error component of this curve recognizable in the region $1.75 \leqslant r \leqslant 5.0$ Å. The latter is the Fourier series termination error mentioned above; larger or smaller values of the coefficient B were found to diminish or increase it.

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[2] Participant in the National Science Foundation's Research Participation for College Teacher's Program, 1965–1966.

[3] See M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **5**, 166 (1959), for example.

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

[5] Some of these values with references are given in Table IV.

[6] O. Bastiansen, O. Hassel, and E. Risberg, *Acta Chem. Scand.*, **9**, 232 (1955).

[7] K. Hedberg and M. Iwasaki, *J. Chem. Phys.*, **36**, 589 (1962).

[8] The data for the curve I_m' have been deposited as Document No. 9779 with ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. A copy may be obtained by citing the document number and by remitting $1.25 for photoprints or $1.25 for 35-mm microfilm. Advance payment is required. Make checks or money order payable to Chief, Photoduplication Service, Library of Congress.

[9] H. P. Hansen, F. Herman, J. D. Lea, and S. Skilman, *Acta Cryst.*, **17**, 1040 (1964).

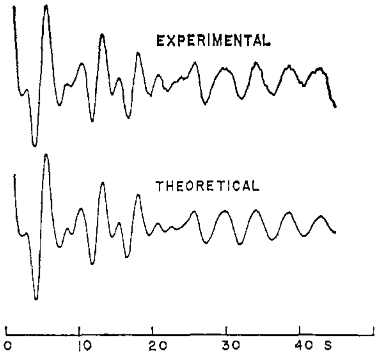

Figure 1. Intensity curves in form I_m'. The theoretical curve corresponds to model of refinement G.

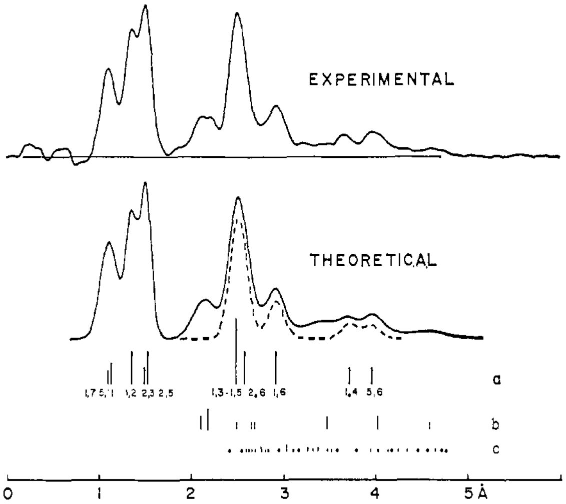

Figure 2. Radial distribution curves. The theoretical curve corresponds to model of refinement G. Group a comprises all C···C and C–H bond distances; b, all nonbond C···H distances except those involving methyl H's subject to methyl group rotation; and c, all rotation-sensitive methyl H···C distances. The dashed theoretical curve corresponds to nonbond C···C distances only, the solid theoretical curve to all distances.

The principal peaks of the experimental curve are largely due to carbon–carbon distances and to the C–H bond distances. The magnitudes of these distances are indicated in Figure 2 by the vertical bars of group a; their correspondence to the molecule may be established by the atom numbering shown in Figure 3. The experimental curve revealed that the molecule is essentially coplanar *trans:* a *cis* configuration cannot be made to fit the region $r > 3.5$ Å and at the same time preserve the fit at smaller r values.[10] Further study, which included the calculation of theoretical radial distribution curves for comparison with the experimental one, gave for the principal parameters the approximate values shown in the second column of Table II.

Refinements of the Structure. Structure refinements were carried out by the method of least squares applied to intensity curves,[11] weighting all observations equally.

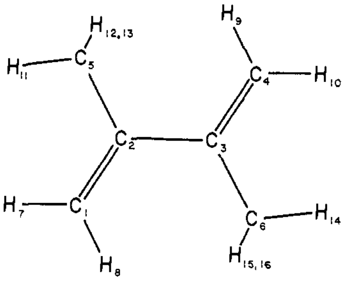

Figure 3. Configuration and atom numbering of 2,3-dimethylbutadiene.

These refinements were designed to explore the questions of methyl group orientation and of twist about the C_2C_3 conjugated single bond as well as the usual matters of bond distance and bond angle values.

It was clear at the outset that it would be impossible to refine simultaneously the ten geometrical parameters (corresponding to a model of symmetry C_2 with symmetric methyl and methylene groups) and vastly greater number of vibrational amplitude parameters. Experience has shown, for example, that a pair of geometrically nonequivalent distances differing in magnitude by only a few hundredths of an angstrom are so strongly correlated with the associated amplitudes of vibration that the refinement fails to converge. For 2,3-dimethylbutadiene this problem turns particularly on (1) the bond distances of type C_2C_3 and C_2C_5, and C_1H_7 and C_5H_{11}, and their associated amplitudes; and (2) the nonbond distances of type C_1C_3 and C_2C_6, and C_2H_7 and C_2H_{11}, and their associated amplitudes. Besides these examples of parameters incapable of simultaneous refinement (despite their being well represented in the diffraction data), there are vibrational amplitude parameters the values of which are very insensitive to the refinement because the distances to which they correspond are of low weight. Examples are the longer C···H amplitudes.

Our choices for the important geometrical parameters of 2,3-dimethylbutadiene are given as the first 14 items of the first column of Table I. Some of these choices were a matter of convenience. For example, it was found more convenient to describe the two C–H and the two C–C single bonds in terms of weighted average values and a split, $\Delta(C–H) = C_5H_{11} - C_1H_7$ and $\Delta(C–C) = C_2H_5 - C_2H_3$, than to use the distances themselves. Many refinements were carried out, characterized by various assumptions applied to certain of these parameters and to the longer C···C and C···H vibrational amplitudes. These assumptions, or refinement conditions, are mostly deducible from Table I which contains the results for a number of selected refinements. The assumptions about the longer C···C and C···H amplitudes are not given for reasons of space; however, the values assigned were essentially those shown for model G in Table II (our final results are based on model G). The following section will help to clarify the content of Table I.

Results

Some features of Table I are particularly striking. The constancy of the values for the C=C double-bond length (essentially independent of refinement conditions) suggests a particularly good determination.

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(10) This result is in accord with the absence of a microwave spectrum for the molecule; see D. R. Lide, Jr., and M. Jen, *J. Chem. Phys.*, 40, 252 (1964). Small amounts of a *cis* configuration can certainly not be ruled out. However, since no *cis* isomer seems to have been detected in any of the substituted butadienes, we have carried out our analysis of the present case assuming it to be absent.

(11) K. Hedberg and M. Iwasaki, *Acta Cryst.*, 17, 529 (1964).

Table I. Results from Different Refinement Conditions

Structural feature	Refinement[a] A	B	C	D	E	F	G
C=C	1.349	1.348	1.348	1.348	1.348	1.348	1.349
C—C$_{av}$	1.504	1.504	1.504	1.504	1.504	1.504	1.504
Δ(C—C)	(0.000)	(0.000)	(0.000)	(0.000)	(0.000)	(0.000)	(0.020)
C-H$_{av}$	1.111	1.110	1.109	1.109	1.109	1.109	1.111
Δ(C—H)	(0.000)	(0.000)	(0.000)	(0.000)	(0.000)	0.033	(0.030)
∠C$_1$=C$_2$—C$_3$	121.35	121.36	121.62	121.44	121.45	121.56	121.98
∠C—C—C	117.86	118.02	117.84	117.82	117.82	117.91	117.87
∠twist[b]	(0.00)	(0.00)	(0.00)	3.12	3.06	(0.00)	(0.00)
∠C=C—H	120.39	(120.39)	(120.4)	(120.4)	(120.4)	(120.4)	(120.4)
∠C—C—H	108.7	(108.7)	(110.4)	(110.4)	(110.4)	(110.4)	(110.4)
$l_{C=C}$	0.0406	0.0406	0.0408	0.0408	0.0408	0.0407	0.0407
l_{C-C}	0.0457	0.0461	0.0459	0.0459	0.0459	0.0459	0.0433
l_{C-H}	0.0838	0.0837	0.080	0.0800	0.0800	0.0800	0.0805
Methyl H	0[c]	3[d]	9[e]	9[e]	9[e]	9[e]	9[e]
Function	I_m'	I_m'	sI_m	sI_m	I_m'	sI_m	I_m'

[a] Distances and root-mean-square amplitudes (*l*) in Å, angles in deg. Parenthesized values were assumed. [b] Refers to rotation about C$_2$C$_3$. [c] All C···H distances longer than through one bond angle omitted. [d] Nonrotating, normal methyl group; all C···H distances included. [e] Rotating methyl group simulated by nine "one-third" H atoms (see text); all C···H distances included.

Table II. Structural Results for 2,3-Dimethylbutadiene[a]

Distance or angle	Exptl radial distribution	Refinement G[b]					
		r	σ_1	σ_T	l	σ_1	σ_T
C=C	1.36	1.349	0.002	0.003	0.040_7	0.002	0.003
C—C$_{av}$		1.504	0.002	0.003			
Δ(C-C)		(0.020)					
C$_2$C$_3$	1.50	1.491	0.002	0.003	(0.0448)		
C$_2$C$_5$		1.511	0.002	0.003	0.043_3	0.003	0.004
C$_1$C$_3$	2.50	2.485	0.009	0.012	(0.0700)		
C$_1$C$_5$		2.480	0.007	0.011	(0.0700)		
C$_2$C$_6$		2.572	0.008	0.011	0.0700)		
C$_1$C$_6$	2.93	2.918	0.010	0.015	(0.0750)		
C$_1$C$_4$	3.66	3.710	0.012	0.017	(0.0750)		
C$_5$C$_6$	3.96	3.946	0.010	0.015	(0.0800)		
C—H$_{av}$		1.111	0.005	0.007			
Δ(C-H)		(0.030)					
C$_5$H$_{11}$	1.10	1.123	0.005	0.007	(0.0800)		
C$_1$H$_7$		1.093	0.005	0.007	0.080_5	0.010	0.014
C$_2$H$_{11}$	2.15	2.174	0.004	0.006	(0.1100)		
C$_2$H$_7$		2.123	0.003	0.005	(0.1100)		
C$_5$H$_9$		2.527	0.018	0.025	(0.1200)		
C$_5$H$_7$		2.686	0.012	0.017	(0.1200)		
C$_2$H$_9$		2.711	0.015	0.022	(0.1200)		
C$_2$H$_{10}$		3.481	0.008	0.011	(0.1200)		
C$_5$H$_8$		3.484	0.007	0.010	(0.1200)		
C$_5$H$_{10}$		4.010	0.012	0.016	(0.1200)		
C$_1$H$_9$		4.053	0.016	0.022	(0.1200)		
C$_1$H$_{10}$		4.604	0.010	0.015	(0.1200)		
C$_{1,3,4,6}$H$_{Me}$		2.54–4.75			(0.2000)		
∠C$_1$=C$_2$—C$_3$		121.98	0.77	1.04			
∠C—C—C		117.87	0.53	0.74			
∠C=C—H		(120.4)					
∠C—C—H		(110.4)					

[a] Distances (*r*) and root-mean-square amplitudes (*l*) in Å, angles in deg. Parenthesized values were assumed. [b] See text and Table I for specifications of refinement conditions.

Similarly, the weighted averages of the lengths of the two types of C–C single bonds, and of the C–H bonds, are well determined, subject to the reasonable assumption that the associated vibrational amplitudes in each case are nearly the same. The values of the two types of C–C–C angles also seem to be well determined, subject to the same assumption. Conclusions about the remaining parameter values are less clear-cut but may be discussed as follows.

Δ(C–C), the Carbon–Carbon Single-Bond Difference. Because the value for this parameter and the values of the amplitudes of the C–C single bonds are so strongly correlated, the refinements were carried out by assuming a value for Δ(C–C) and, when this was different from zero, for one of the amplitudes (refinement G). Only positive values of Δ(C–C), which corresponds with common experience about the lengths of these two types of carbon–carbon single bonds, were tested. Refinements A–F reveal an unusual circumstance: the vibrational amplitude, even with no split assumed, is several per cent *smaller* than the corresponding amplitude for comparison molecules (Table IV). Any actual difference between the lengths of the two types of C–C single bonds must be accompanied by a further decrease in these amplitudes, as is seen in refinement G. This effect was tested by three other refinements, which

Table III. Error Matrix ($\times 10^6$) for 2,3-Dimethylbutadiene[a]

$l_{C=C}$	l_{C-C}	l_{C-H}	C=C	C—C$_{av}$	C—H$_{av}$	C_1C_3	C_1C_5	C_2C_6	C_1C_4
4.282	−0.456	0.170	−0.002	0.985	−0.950	−0.801	1.882	2.486	−1.472
	6.529	1.964	−1.473	0.571	−0.684	−1.282	−0.920	1.751	−3.018
		93.71	1.574	0.630	−14.57	−5.943	3.544	8.175	−7.072
			4.396	−0.036	1.095	−1.141	5.709	3.312	1.680
				2.717	−0.293	−0.354	5.162	4.739	−1.594
					22.64	2.016	0.185	−1.481	3.615
						76.45	−40.80	−45.82	101.7
							55.64	15.87	−52.60
								58.27	−60.90
									138.2

C_2H_{11}	C_2H_7	C_5H_7	C_2H_9	C_1H_9	C_1H_{11}	C_4H_{11}	∠C_1=C_2—C_3	∠C—C—C
−0.474	−0.063	1.933	−2.607	−2.761	1.600	−0.674	−140.4	59.33
−0.667	−1.594	−1.659	−2.263	−3.806	−1.077	0.197	−43.67	57.40
−4.332	2.546	−0.932	−17.24	−16.60	−4.044	−9.701	−659.0	527.1
−0.408	3.339	8.103	−3.527	0.658	6.000	−0.043	−410.6	250.6
−0.196	−0.086	6.197	−3.091	−3.366	5.614	−0.681	−229.5	6.247
3.397	−3.130	8.846	12.27	14.24	11.85	16.19	111.8	−72.73
35.53	23.44	−66.66	131.4	134.4	−47.55	55.74	6,519	−3,359
−18.83	−8.205	86.22	−76.38	−73.44	64.25	−63.57	−4,218	522.0
−21.33	−11.64	20.46	−84.08	−83.72	16.42	2.931	−4,435	3,726
47.39	33.87	−85.92	174.7	181.9	−61.61	74.93	8,529	−4,321
16.78	10.49	−29.83	62.03	63.62	−20.67	27.51	3,024	−1,560
	11.29	−16.30	37.04	41.34	−12.60	14.70	1,731	−853.8
		138.8	−118.8	−114.7	104.6	−99.46	−6,637	731.2
			232.3	236.4	−83.68	101.7	11,500	−5,853
				244.8	−80.44	105.2	11,470	−5,791
					80.58	−67.76	−4,839	505.7
						113.3	4,728	304.4
							593,400	−300,300
								276,000

[a] Distances and root-mean-square amplitudes in Å, angles in deg.

together with G, gave the Δ(C–C) and corresponding l_{C-C} values 0.000 and 0.0459 Å., 0.020 and 0.0433 Å, 0.040 and 0.0377 Å, and 0.056 and 0.0334 Å.[12] From these data, taking into account the value $2\sigma = 0.007$ Å for the amplitude l_{C-C}, we conclude that the split Δ(C–C) is not likely to be greater than about 0.03 Å.

Δ(C–H), the Carbon–Hydrogen Bond Difference. The procedures used were similar to those used for the study of Δ(C–C). When the difference between the lengths of the methylene and methyl C–H bonds was assumed to be zero, the best value for the amplitudes of vibration (assumed equal) was found to be 0.0838 Å (refinements A and B). This value is larger than those generally found for C–H bonds; when the more likely value 0.0800 Å was assumed for these amplitudes, the value Δ(C–H) = 0.033 Å was obtained (refinement F). These results are completely compatible with the expected difference between the lengths of the two bond types and the expected vibrational amplitude(s) for these bonds. However, the significance of the experimental results is doubtful ($2\sigma = 0.028$ Å for l_{C-H}) and perhaps little point should be made of them.

Twist Angle, Torsion about C_2C_3. Initially, it had seemed possible that some twist about the bond C_2C_3 might occur as a consequence of steric interaction of the methyl and methylene groups. The lack of any such indication in the radial distribution curves led us to attempt refinements of the twist angle only for the purpose of obtaining error information. Refinements D and E gave estimates of 3° for the twist angle, a value less than half the standard error (not shown). There is thus no evidence of a departure of the carbon skeleton of the molecule from coplanarity.

∠C=C—H and ∠C—C—H. The distances most important for determining these angles give rise to the peak at 2.16 Å. It was found that the distances did not, in general, refine to values corresponding to plausible angles. It was necessary, therefore, to give the angles the reasonable, fixed values shown in Table I.

Methyl Group Orientation. No attempt was made to include methyl group orientation as a refinable parameter. In the earlier refinements, these groups were assumed to be staggered with respect to the methylene hydrogen atoms (refinement B). However, the theoretical radial distribution curve for this model did not agree well with the experimental curve in the region of 2.9 Å, and investigation revealed that the disagreement could be attributed to the longer methyl H···C distances. In order to reduce the disagreement, less restricted rotation of the methyl groups was simulated by introducing nine "one-third" hydrogen atoms located on the circle of rotation at regular intervals in place of the group of three. Plausible amplitudes for the longer C···H distances were then introduced. So far as the parameters of interest were concerned, this procedure gave virtually unchanged results (compare refinements B and C); however, the agreement between the theoretical and experimental radial distribution curves was strikingly improved. We interpret this result as strongly indicating an only slightly restricted rotation of the methyl groups.

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(12) We have found that a single radial distribution curve peak composed of two unresolved Gaussian peaks (corresponding to two interatomic distances) may be fit nearly equally well for $\Delta r/l \leqslant 1$ by sets of parameter values related by the approximate formula $\Delta r/l \simeq (1 + k)[(2/k) \ln (1 + \Delta l/l)]^{1/2}$ Here r and l are distance and amplitude values, Δr and Δl are the difference and change in these quantities, and k is the weight of one distance relative to the other taken as unity. As $\Delta r/l \geqslant 1$ increases, the quality of fit decreases.

Table IV. Comparison of the Structures of 2,3-Dimethylbutadiene and Related Molecules[a,b]

	2,3-Dimethylbutadiene[c]		Butadiene[d]		Isobutylene[e]		Propylene[f]	
	Value	Error	Value	Error	Value	Error	Value	Error
$C{=}C$	1.349	0.006	1.344	0.001	1.331	0.003	1.336	0.004
$C{-}C$	1.491 1.511	0.006 0.006	1.467	0.003	1.505	0.002	1.501	0.003
$C{=}H_2$	1.093	0.007	1.094	0.003	(1.084)		1.081–1.091	0.003
$C{\equiv}H_3$	1.123	0.007	...		1.113	0.004	1.085–1.098	0.003–0.014
$l_{C=C}$	0.040_7	0.006	0.0436	0.001	0.048	0.006	...	
l_{C-C}	(0.0448) 0.043_3	 0.006	0.0513	0.002	0.059	0.006	...	
$l_{C=H_2}$	0.080_5	0.014	0.0821	0.002	(0.102)		...	
$l_{C\equiv H_3}$	(0.0800)				0.079	0.008	...	
∠C=C—C	121.98[g]	1.04	122.9	1.0	...		124.3	0.3
∠C—C—C	117.87	0.74	...		112	...	...	
∠C=C—H	(120.4)		119.5	2.0	(122.2)		119.0–121.5	0.3
∠C—C—H	(110.4)				110.4	1.6	111.2	0.3
Method	Electron diffraction[h]		Electron diffraction[i]		Electron diffraction[j]		Microwave spectroscopy[k]	

[a] Distances (r) and amplitudes (l) in A, angles in deg. [b] Parenthesized values were assumed. [c] Distance and amplitude values are r_a and l_a; errors are $2\sigma_T$. [d] Distance and amplitude values are $r_g(1)$ and $l_g(1)$; errors are 2σ. [e] Distance and amplitude values are r_g and l_g; errors are $2\sigma_T$. [f] Distance values are r_s; errors are "limits of uncertainty." [g] This is $\angle C_1{=}C_2{-}C_3$. [h] This investigation. [i] W. Haugen and M. Traetteberg, *Acta Chem. Scand.*, **20,** 1726 (1966). [j] L. S. Bartell and R. A. Bonham, *J. Chem. Phys.*, **32,** 824 (1960); see also V. W. Laurie, *ibid.*, **34,** 1516 (1961). [k] D. R. Lide and D. Christensen, *ibid.*, **35,** 1374 (1961).

Error Analysis. The errors σ_1 listed in Table II are obtained directly from the least-squares analysis and reflect the agreement between the experimental intensity curve I_m' and the theoretical intensity curve corresponding to the model. They are the square roots of the diagonal elements of the error matrix **M** defined by

$$\mathbf{M} = S^2\mathbf{C}\mathbf{B}^{-1}\mathbf{C}' \qquad (3)$$

where $S^2 = \mathbf{V}'\mathbf{P}\mathbf{V}/(N - m)$, **B** is the matrix of coefficients of the normal equations, and **C** is a matrix which transforms the parameters actually adjusted into the variables of interest.[11] These errors do not include estimates of any systematic effects such as errors in electron wavelength, camera distance, etc. Plausible estimates of these additional errors may be made; they are $0.005r$ for distances and $0.02\langle l_{i,j}^2\rangle^{1/2}$ for amplitudes.[7] An estimate of a total standard error may be obtained by first increasing the random errors by the factor $\sqrt{2}$ (to take partial account of possible correlation among the observations) and combining these with the estimates of systematic error in the usual way. The results are given in Table II as σ_T.

An abbreviated form of the error matrix **M** is shown in Table III. This matrix is of most use in deduction of correlations among the many variables: for the reasons given above, it does not provide a realistic estimate of the errors themselves.

Summary of Results. Gaseous 2,3-dimethylbutadiene is essentially *trans*, with a coplanar heavy atom skeleton to within about 9° (1σ) twist about the conjugated single bond. Methyl group rotation is essentially free, and the lengths of the two types of single bonds probably do not differ by more than 0.03 Å. An unbiased expression of our findings for the more important distances (r_a), angles, and amplitudes (l_a) is given in Table II as refinement G, which is based on assumed C_{2h} symmetry, symmetric $C{=}CH_2$ and $C{-}CH_3$ groups, $\Delta(C{-}C) = 0.02$ Å, and $\Delta(C{-}H) = 0.03$ Å. The error matrix (Table III) is also an important part of our results.

Discussion

The structure of 2,3-dimethylbutadiene is not unusual. The several bond distances and bond angles have values about as expected from consideration of molecules with similar structural features (Table IV). Some small anomalies do exist, such as the C=C bond length and the methyl and methylene C—H bond lengths which, at 1.349, 1.123, and 1.093 Å, respectively, are longer than their counterparts in other molecules. However, it is doubtful that the differences are significant.

Comparison of our results with those of butadiene itself raises an interesting and puzzling question about the conjugated C-C single bond. The length of this bond is apparently about 0.024 Å shorter in butadiene, an amount which seems to be statistically significant. An inductive effect which would increase the σ electron density on the central carbon atoms of the dimethyl compound at the expense of the methyl groups accounts qualitatively for the observation. However, a simple self-consistent field molecular orbital calculation for the two molecules (kindly carried out for us by Professor G. J. Gleicher), which might be expected to give a fair quantitative indication of any difference, led to a difference of only 0.001 Å. Some of the observed bond elongation might be attributed to nonbonded repulsions of greater magnitude in the dimethyl compound, but the rather freely rotating methyl groups and the $C_1{=}C_2{-}C_3$ bond angle, which is nearly equal to that in butadiene, suggest that this effect cannot be important.