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An Electron Diffraction Investigation of Dimethylketene Dimer*

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An electron diffraction investigation of dimethylketene dimer confirms the 2,2,4,4-tetramethylcyclobutadione-1,3 structure. The following parameters were determined for the symmetrical model: C−C (ring) = 1.56±0.05A, $C-CH_3 = 1.54 \pm 0.05$A, C=O = 1.22±0.04A, ∠C−CO−C = 93°±6°, and $\angle CH_3-C-CH_3 = 111° \pm 6°$. The limits of error assigned to the angles apply only if simultaneous variation is excluded; otherwise much larger limits must be assigned. A notable feature of the structure is the large temperature factor which must be ascribed to the interatomic distances greater than 3A. The relation of this temperature factor to the unusually large atom polarization is discussed in terms of the probable amplitudes of the pertinent modes of vibration of the molecule.

THIS investigation of the molecular structure of dimethylketene dimer, which may be presumed to be 2,2,4,4-tetramethylcyclobutadione-1,3, was undertaken because of its interest in connection with the structure of diketene, which is still under active discussion. Although work on diketene was begun, it was discontinued because our diffraction photographs were unsatisfactory and because it was understood that an electron diffraction investigation is forthcoming from another laboratory.[1]

EXPERIMENTAL

The sample of dimethylketene dimer was prepared by Dr. C. W. Smith of the Shell Development Company, Emeryville, California. Dimethylketene [$(CH_3)_2C=C=O$], prepared from α-bromoisobutyryl bromide, was isolated and then allowed to polymerize in ethyl acetate solution. The dimethylketene dimer which was separated from this mixture melted at 113°–114°C. A rough determination of its vapor pressure gave the values 6 mm at 52°C and 38 mm at 87°C. These characteristics are in agreement with those reported[2,3] in the literature for samples obtained by different syntheses. As might be expected the compound has no permanent dipole moment.[2,3] Diketene, on the other hand, has a dipole moment[4] of 3.31 D, and so cannot have the cyclobutadione-1,3 structure.

The electron diffraction investigation was carried out with the apparatus described by Brockway.[5] Photographs were taken at a camera distance of 10.93 cm with electrons of wavelength 0.0610A as determined by standardization against zinc oxide.[6] The vapor was obtained from a sample of the substance heated at 90° to 120°C in a high temperature nozzle.[7]

INTERPRETATION

Both the radial distribution method[8] and the correlation method[9] were used in interpreting the photographs. The radial distribution function was calculated[10] from the visual intensity curve by means of the equation

$$rD(r) = \sum_{q_i=1,2,\cdots,100} I(q_i) \times \exp(-aq_i^2) \sin\left(\frac{\pi}{10} q_i r\right), \quad (1)$$

with a so determined that $\exp(-aq_i^2)$ is equal to 0.10 at $q=90$. The theoretical intensity curves used in the correlation treatment were calculated

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from the simplified formula[10]

$$I^0(q)=\sum_{i,j}\frac{Z_iZ_j}{r_{ij}}\exp\left(-b_{ij}q^2\right)\sin\left(\frac{\pi}{10}r_{ij}q\right), \quad (2)$$

where the constant b_{ij} in the exponential temperature factor term was given the value 0.00015 for bonded C—H terms, 0.0003 for non-bonded C···H terms, and 0 for all other terms.

RESULTS

The electron diffraction pattern of dimethylketene dimer is represented by curve V of Fig. 1. The unobservable first feature (dotted portion of curve V), which is relatively insensitive to structure, was taken from the theoretical curves. The radial distribution function R calculated from this visual curve shows sharp peaks at 1.17A, 1.55A, 2.20A, and 2.58A, and rather broad peaks at 3.32A and at 4.43A. Its interpretation in terms of the tetramethylcyclobutadione structure is straightforward. The first peak corresponds to the C—H and C=O terms; with the assumptions that the C—H peak is at 1.09A, that it corresponds to a temperature factor with $b_{C-H}=0.00015$, and that the two terms have the relative weights corresponding to those expected for tetramethylcyclobutadione, this first peak gives a C=O distance of about 1.22A. The peak at 1.55A corresponds to the C—C distances in the four-membered ring and to the C—CH_3 distances. These distances cannot differ greatly because the half-width (at half-height) of this peak corresponds closely with that expected from the use of the exponential term in Eq. (1), namely, $w_{\frac{1}{2}}=8.5/q_{max}$. The peak at 2.20A corresponds to the non-bonded C···H terms and the cross-ring C···C distances. Analysis of this peak with the assumptions C···H=2.16A and $b_{C\cdots H}=0.0003$ yields a C···C distance of 2.21A, which corresponds to a C—C bond distance of 1.56A in the ring, in good agreement with the 1.55A peak. (A strict interpretation would then suggest a C—CH_3 distance of 1.54A.) The peak at 2.58A corresponds to the shortest non-bonded C···O, C···CH_3, and CH_3···CH_3 distances, which have relative weights nZ_iZ_j/r_{ij} of 20, 30, and 8. With consideration of the small width of this peak, these distances, particularly the first two, cannot differ greatly from 2.58A. The remaining comparisons of the distance spectrum of tetramethylcyclobutadione with the radial distribution function (as shown for model A; see Fig. 1) is satisfactory if the terms corresponding to distances greater than 3A are given suitable temperature factors. Thus the terms which contribute to

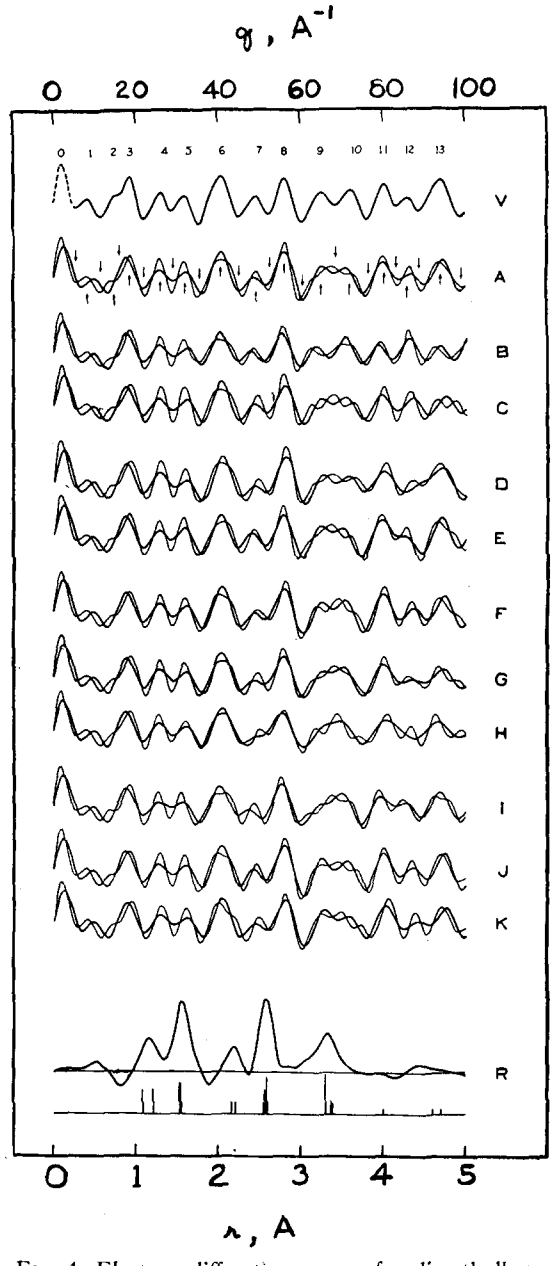

FIG. 1. Electron diffraction curves for dimethylketene dimer: visual curve V, theoretical intensity curves $A\cdots K$, and radial distribution function R. The heavy theoretical curves were calculated (for models defined in the text) omitting distances greater than 3A; in the light curves all distances were included. The numbers above curve V and the arrows on curve A refer to the measured q values in Table I.

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the peak at 3.32A give a composite term at 3.33A, in good agreement with the position and also with the area of this peak, but if the temperature factor is omitted the resulting peak is too narrow and too high as compared with that shown by the radial distribution function. The small peak at 4.43A does not correspond well with the spectrum of the comparatively unimportant long distances in the molecule, but it may indicate in a general way the presence of scattering from these terms. At any rate it can be said that the discrepancies in this region represent errors in the visual curve no greater in magnitude than those demonstrated by the two sharp negative regions at 0.83A and 1.89A, and that the tetramethylcyclobutadione structure is well confirmed by the radial distribution curve.

In the correlation procedure the visual curve was compared with theoretical intensity curves calculated for tetramethylcyclobutadione models of symmetry D_{2h} (except for the hydrogen atoms) with the bonded C−H distance 1.09A and tetrahedral bond angles at the methyl carbon atoms. All hydrogen interaction terms except those due to the bonded and shortest non-bonded carbon-hydrogen distances were omitted, because of their relatively small weight and necessarily severe temperature factors. The five parameters of this structure may be taken as the ratio $(C-C)/(C-CH_3)$, the ratio $2(C=O)/[(C-C)+(C-CH_3)]$, the C−CO−C (ring) angle, the CH_3-C-CH_3 angle, and as size parameter, $[(C-C)+(C-CH_3)]/2$. The temperature factor for the distances greater than 3A also needs to be determined. In order to take account of this temperature factor two theoretical curves were calculated for each model, only the terms less than 3A being included for the additional, heavy curve (Fig. 1). It was found that for the best models the most satisfactory agreement with the visual curve was obtained by interpolation[11] between the heavy and light curves according to the temperature factor $\exp(-b_{ij}q^2)$ for distances greater than 3A with b_{ij} equal to 0.0006. An upper limit of $b_{ij}=0.0008$ can be determined by the requirement that the second maximum (Fig. 1) be adequately resolved from the third maximum, while a lower limit of $b_{ij}=0.0004$ may be arrived at by the requirements that the fourth and fifth maxima be somewhat weak as compared with the sixth maximum, and that the ninth and tenth maxima shall remain two resolved peaks of approximately equal intensity instead of becoming a triple peak. On the basis of these considerations and the analysis of the width of the 3.3A peak of the radial distribution function in terms of the distances for the various models and the temperature factor, we believe that the value of $b_{ij}=0.0006$ cannot be in error by more than about ±30 percent.

Model A, which was suggested by the radial distribution function, is defined by the parameters $2(C=O)/[(C-C)+(C-CH_3)]=1.22/1.55$, $(C-C)$ ring$/(C-CH_3)=1.56/1.54$, $\angle$C−CO−C (ring) $=90°$, $\angle CH_3-C-CH_3=109°\ 28'$, and $[(C-C)+(C-CH_3)]/2=1.55$A, and leads to curves A in excellent agreement with the visual curve V in the sense of the interpolation just described. The slight discrepancy in regard to the relative intensities of the ninth and tenth maxima is discussed below. Re-examination of the photographs indicated that the differences in the third, fourth, fifth, and sixth maxima were exaggerated slightly in the drawing of the visual curve, and that the interpolated theoretical curve is actually in good agreement with the photographs in these respects.

A complete examination of all possible parameter variations in the neighborhood of model A was not undertaken, although each of the parameters was varied separately in the following series of models, in which, unless otherwise stated, the parameters have the same values as in model A. In considering the effects on the curves of parameter variation it was found useful throughout to think in terms of the radial distribution function. Variation of $(C-C)/(C-CH_3)$ to 1.61/1.49 and to 1.51/1.59 is illustrated by curves B and C; it appears that for this variation models with these two distances differing by as much as 0.09A are definitely inacceptable, particularly with regard to the relative intensities of the extreme outer features. Models D and E, with $2(C=O)/[(C-C)+(C-CH_3)]$ equal to

[11] The interpolated curve lies 13 percent of the way from the light toward the heavy curve at $q=15$; 42 percent at $q=30$; and 95 percent at $q=70$. For the best model the three distances contributing to the 3.3A peak are nearly equal. Some of the less satisfactory models tend to require somewhat different values of b_{ij}; for example, models with these distances distributed about 3.3A as an average require smaller values of b_{ij}.

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1.17/1.55 and 1.27/1.55 are somewhat outside of the range of acceptability. Of the three models, *F*, *G*, and *H*, in which the C−C−C angle at the carbonyl group was given the values 85°, 95°, and 100°, *F* and *G* are nearly acceptable, while *H* is definitely poor. Of models *I*, *J*, and *K*, in which the CH_3-C-CH_3 angle was given the values 100°, 115°, and 120°, the only acceptable model is *J*.

Simultaneous variations of the parameters were investigated by inspection of the curves on the assumption that the effects of the variations are additive, as they must be for small variations. Combinations of variations of $(C-C)/(C-CH_3)$ and $2C=O/[(C-C)+(C-CH_3)]$ do not lead to better agreement than that shown in curve *A*, as may be seen by comparisons of curves *B*, *C*, *D*, and *E*; neither do they suggest that simultaneous variations of these parameters could lead to satisfactory models with parameters outside the ranges of acceptability established for the single variations. The same is true, moreover, for combined variations of these two parameters with either one of the angles. However, when simultaneous variations of the two angles are allowed a much increased range of acceptable angle values is revealed in which the angles are increased or decreased together. This is illustrated by an average of curves *G* and *J* with somewhat the greater weight for *G*. Indeed, slightly better agreement with the relative intensity of the ninth and tenth maxima than shown by model *A* is obtained by a variation in the direction of this combination without producing unsatisfactory effects elsewhere. On the other hand, simultaneous increase of one angle and decrease of the other leads very quickly to unsatisfactory curves.

On the basis of the radial distribution function, these considerations, and quantitative comparison of observed and calculated q values for models *A* (Table I), *C*, *E*, *G*, and *J* the final parameters were taken as C−C=1.56A, $C-CH_3$ =1.54A, C=O=1.22A, ∠C−CO−C=93°, and ∠CH_3-C-CH_3=111°. Although the average of C−C and $C-CH_3$, which determine the position of the 1.55A peak of the radial distribution function, can be determined with the usual precision (±0.02A), their difference cannot, the two distances being so nearly alike as to be unresolvable; this circumstance makes it necessary to assign the considerably larger value ±0.05A for the limits of error (limits which we believe the error is not likely to exceed) of the separate determination of these two distances. The C=O distance, with the limits of error of ±0.04A, is also not well fixed because all of the oxygen terms are either unimportant or imperfectly resolved from other terms. Limits of ±6° can be assigned to the angle variations if simultaneous variation of the two angles is excluded; otherwise much greater limits of error, so great as almost to deprive the experimental values of any quantitative significance, must be assigned.

TABLE I.

Min.	Max.	q obs.	q calc.[a]	q calc./q obs.
1		5.32	5.5	(1.034)
	1	8.25	8.1	(0.982)
2		11.60	11.4	(0.983)
	2	14.81	14.7	(0.993)
3		16.13	15.6	(0.967)
	3	18.58	18.5	0.996
4		22.07	22.0	0.997
	4	26.09	25.8	0.989
5		28.68	28.8	1.004
	5	31.87	31.8	0.998
6		35.35	35.5	1.004
	6	40.64	40.7	1.001
7		44.95	45.5	1.012
	7	49.15	49.1	0.999
8		52.41	51.8	0.988
	8	55.90	55.9	1.000
9		60.50	60.5	1.000
	9	65.02	65.2	1.003
10		68.37	68.0	0.995
	10	72.02	70.9	0.984
11		76.30	75.3	0.987
	11	80.28	80.0	0.997
12		83.24	83.9	1.008
	12	86.06	86.7	1.007
13		88.66	90.0	1.015
	13	93.94	94.3	1.004
14		98.91	98.9	1.000
			Average	0.999
			Average deviation	0.006

[a] The values of q_{calc} were taken from the average curve obtained by weighting the light and heavy curves of model *A* according to the factor exp (-0.0006_q^2). Values in parentheses were omitted in the calculation of the average and average deviation.

TEMPERATURE FACTOR AND ATOM POLARIZATION

The tetramethylcyclobutadione molecule is so complex that any simple consideration of the vibrations responsible for the anomalously large temperature coefficient, which represents an increment to the average that prevails for the shorter distances in the molecule, is likely to be unsatisfactory. Indeed, our estimate of the temperature factor coefficient is not itself very precise. We wish, nevertheless, to discuss a

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particular mode of vibration which we believe may be mainly responsible both for the anomalous temperature factor of the longer distances and the unusually large atom polarization,[3] which corresponds to a root-mean-square dipole moment of about 0.7 D. Coop and Sutton[3] concluded that a mode of vibration different from that which we propose was responsible for the anomalous atom polarization. For each of these two modes of vibration we shall compare the root-mean-square amplitude required for the anomalous temperature factor, and that required for the anomalous atom polarization, with estimates of the amplitudes to be expected on the basis of classical temperature excitation.

The first-mentioned mode of vibration is the one in which, approximately, the $\diagdown C{=}O \diagup$ groups oscillate in a plane perpendicular to that of the ring while the $\diagdown C(CH_3)_2 \diagup$ groups move similarly and in the opposite direction, each of the groups retaining its two planes of symmetry and the four bond angles in the ring remaining equal. If the coefficient $b_{ij}=0.0006$ can be said to apply to the $CH_3\cdots O$ distances, as is reasonable since these are by far the most important of the long distances, for which b_{ij} was derived as an average[12] value, the root-mean-square deviation, θ, of the $C{=}O$ bonds from the mean plane of the molecule, is 5°. The atom polarization of the gas molecule corresponds to a root-mean-square dipole moment of 0.66 D. Reduced to 0.6 D to allow for the "normal" atom polarization (5 percent of P_E) which might be expected for the simpler group vibrations, this moment corresponds to a value of 7° for θ, in fair agreement with the diffraction data estimate. That these amplitudes are reasonable for this mode of vibration can be seen from a calculation of the amplitude for classical excitation at 100°C on the assumption of a parabolic potential function[13] for bending of the ring bond angles from an (assumed) normal angle ϑ_0 of $109\frac{1}{2}°$. This amplitude, $\theta=3.5°$, is smaller than the values derived above. It may be remarked, however, that the expected anharmonicity of the potential function would lead to a considerable increase of the estimate, the ring bond angles being greatly strained from their normal tetrahedral values.

Coop and Sutton[3] attributed the atom polarization predominantly to oscillations of the $C{=}O$ groups in the plane of the four-membered ring. In order to account for the b_{ij} value of 0.0006 by this mode of vibration alone a root-mean-square displacement, θ', of the $C{=}O$ bond of 14° is required. The anomalous atom polarization requires a value of θ' of 10° if the two $C{=}O$ groups are assumed to oscillate independently. With the assumption of a constant of 10^{-11} erg/radian^2 for bending the $C{=}O$ bond against the rest of the $C{-}CO{-}C$ group, the amplitude calculated for classical excitation is found[14] to be $\theta'=2°$.

These calculations show that the very large temperature factor for the long distances in dimethylketene dimer is of the right order of magnitude to be consistent with the anomalous atom polarization. They further suggest that both of these effects may well arise predominantly from an out-of-plane vibration of the ring atoms and the attached groups rather than from vibrations of the oxygen atoms in the plane of the ring as suggested by Coop and Sutton. To be sure the argument is based on force constant estimates which are none too reliable; however, it seems unlikely that they can be so greatly in error as to invalidate the conclusion.

ACKNOWLEDGMENT

We wish to thank Professor Linus Pauling for his interest and encouragement, and Dr. Robert Rasmussen of the Shell Development Company for his courtesy in providing us with the sample of dimethylketene dimer.

[12] Only the 3.3A group of distances is important. If for this group account were taken of the relatively small dependence of the $CH_3\cdots C$ (ring) and $O\cdots C$ (ring) distances on this vibration as compared with that of the $CH_3\cdots O$ distances this estimate of θ would be slightly increased; however, for a model with distances in the 3.3A region not all alike (reference 11) it would be somewhat decreased.

[13] The constant $k=10^{-11}$ erg/radian^2/bond angle in the potential function $2V=k(\delta\vartheta_{C-C-C})^2$ was estimated from the bending frequency of propane.

[14] The bending constant used here for $C{=}O$ against the $C{-}C{-}C$ group suggests itself as a reasonable lower limit in view of the bond bending constants listed by Herzberg (*Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 193), at least if it is assumed that the bond angle strain in the four-numbered ring has no great effect on this constant. With this force constant the estimated frequency of the vibration is low enough (about 300 cm^{-1}) that the assumption of classical excitation cannot be greatly in error.

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