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THE MOLECULAR STRUCTURE OF TRIMETHYLENECYCLOPROPANE

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Abstract The molecular structure of trimethylenecyclopropane has been determined from electron diffraction data obtained on the vapor. Planarity of the molecule was assumed and shrinkages were calculated from the evaluated non-bonded C—C distances. The geometric parameters calculated by least squares from the molecular intensity [qM(q)] are:

$$C{=}C = 1{\cdot}343 \pm 0{\cdot}02\,\text{Å}; \; C{-}C = 1{\cdot}453 \pm 0{\cdot}02\,\text{Å}, \; C{-}H = 1{\cdot}108 \pm 0{\cdot}015\,\text{Å}; \; \angle CCH = 121{\cdot}8 \pm 2°.$$

The calculated shrinkages are: $\delta_{C_1C_4} = 0{\cdot}009$ Å; $\delta_{C_2C_4} = 0{\cdot}028$ Å. The uncertainties quoted for the distances are twice the calculated standard deviations. A variation of Walsh's model for the bonding in cyclopropane is proposed, to account for reported differences in bond lengths between trimethylenecyclopropane and several related molecules. The structural data suggest that delocalization is present in these 3-member rings.

INTRODUCTION

TRIMETHYLENECYCLOPROPANE[1,2] provides a unique opportunity for a structural study since it is one of the two known C_6H_6 isomers with D_{3h} symmetry. The significance of this structural type is underlined by several theoretical analyses[3,4] which appeared in the literature prior to its initial synthesis. Subsequent preparations of the compound[1,2] and of its hexamethyl derivative[5] provided the possibility for checking these predictions. In view of the current interest in the chemistry of trimethylenecyclopropane and of its derivatives the need for a precise structure determination is apparent.

ANALYSIS AND RESULTS

The experimental intensity and the best background are reproduced in Fig. 1. The experimental molecular intensity $(\pi/10)\,qM_{exp}(q)$ is sketched in Fig. 2, and the experimental distribution curve, as calculated with a damping factor, $\exp[-0.00536\,(\pi^2/100)q^2]$, is given in Fig. 3.

The IR spectrum of TMCP has frequencies characteristic of C—C and C═C; also, their assignment is compatible with D_{3h} symmetry.[13] Hence it is planar. Experimental diffraction data from planar molecules cannot be satisfied by planar models unless corrections for shrinkage in the nonbonded distances are included.[14,15] In molecules like TMCP, where angles are determined by symmetry, the shrinkage factors can be determined experimentally.

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Practical shrinkages δ_p were estimated for the nonbonded carbon–carbon distances by a modification of the method of Morino *et al.*[16] Since the peaks due to the nonbonded distances were not resolved in the radial distribution curve, the $r_g(0)$ interatomic distances could not be determined from them. The procedure adopted was to assume a nonplanar model and to refine it by least squares, so that it fitted the $M_{exp}(q)$ curve. The distances obtained from this model were then used to calculate the shrinkages (numbering of the atoms is indicated in Fig. 4),

$$-\delta_{16} = r_{16} - [r^2_{C-C} + r^2_{C=C} - 2r_{C-C}r_{C=C}\cos 150°]^{\frac{1}{2}}$$

and

$$-\delta_{26} = r_{26} - [2r_{C=C}\cos(\pi - 150°) + r_{C-C}].$$

The magnitudes $r_{C=C}$, r_{C-C}, r_{12}, and r_{26} are $r_g(0)$ values evaluated from

$$r_g(0) = r_a(1) + l^2/r_g(1).$$

Here, the $r_g(1)$ values were obtained from bond lengths and valence angles computed by least squares, assuming that neglecting the anharmonicity correction in $M_{theor}(q)$ is of no consequence. Because of the D_{3h} symmetry, the angle contained by $r_{C=C}$ and r_{C-C} is 150°.

The "best set" of interatomic distances and shrinkage factors is given in the left column of Table 1. The assigned limits of error are approximately twice the standard

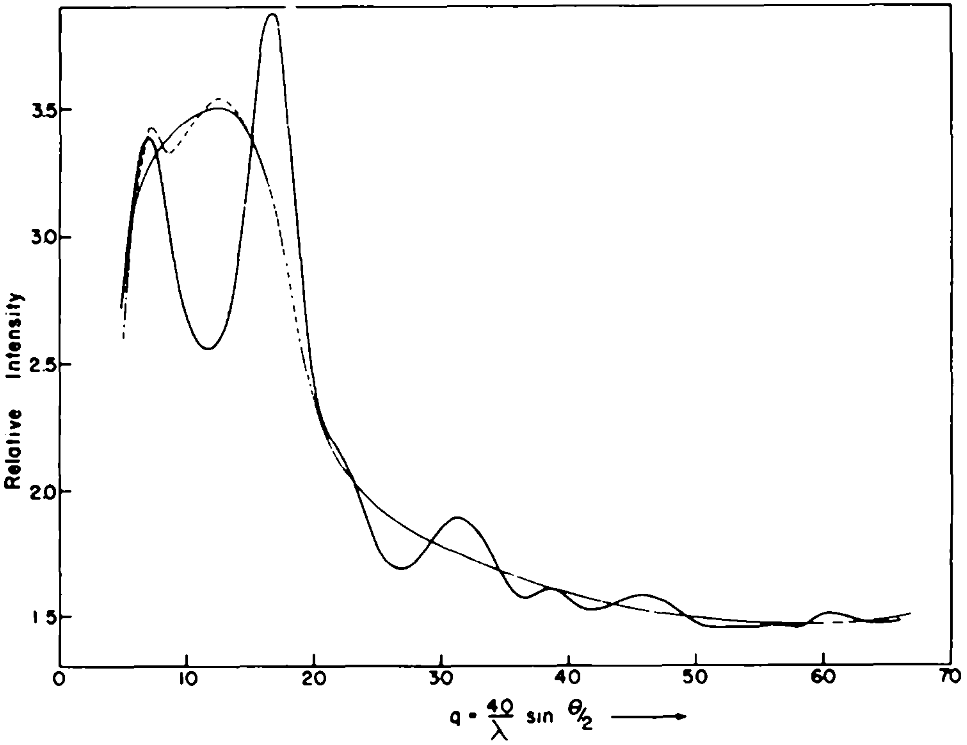


FIG. 1 The experimental intensity (heavy line) and the best smooth background for the refined model. For 7 < q < 14 the particular sector used had an undulation for which a correction was inserted, as indicated by the dashed curve.

deviations. The refined parameters listed in the right-hand column were calculated for a planar model (no shrinkage). However, the constraint to planarity is not a physically realizable condition because it does not include averages of non-bonded distances over their out-of-plane vibrations. The "shrinkage effect" appears because the measured distances in the "weighted average structure" are averages over *all* the molecular vibrations. Theoretical $(\pi/10)qM(q)$ curves for both models are sketched in Fig. 2, and the resolution of the radial distribution curve, in terms of atom-pair contributions according to the "non-planar" model is given in Fig. 3. The lower "error curve" in the latter figure is the difference between the experimental curve and that calculated from $(\pi/10)qM(q)$ for the planar model including shrinkage. The corresponding error matrix is reproduced in Table 2, wherein the diagonal elements are the calculated uncertainties for the listed parameters. The constrained parameters (labeled in Table 1) were not included. Some constraints had to be imposed because allowing full freedom of variation for all parameters simultaneously led to completely unreasonable values for the root-mean square displacements. This is due partly to the limited amount of data available for this structure determination and partly to the large off-diagonal elements in the $[B]^{-1}$ matrix.

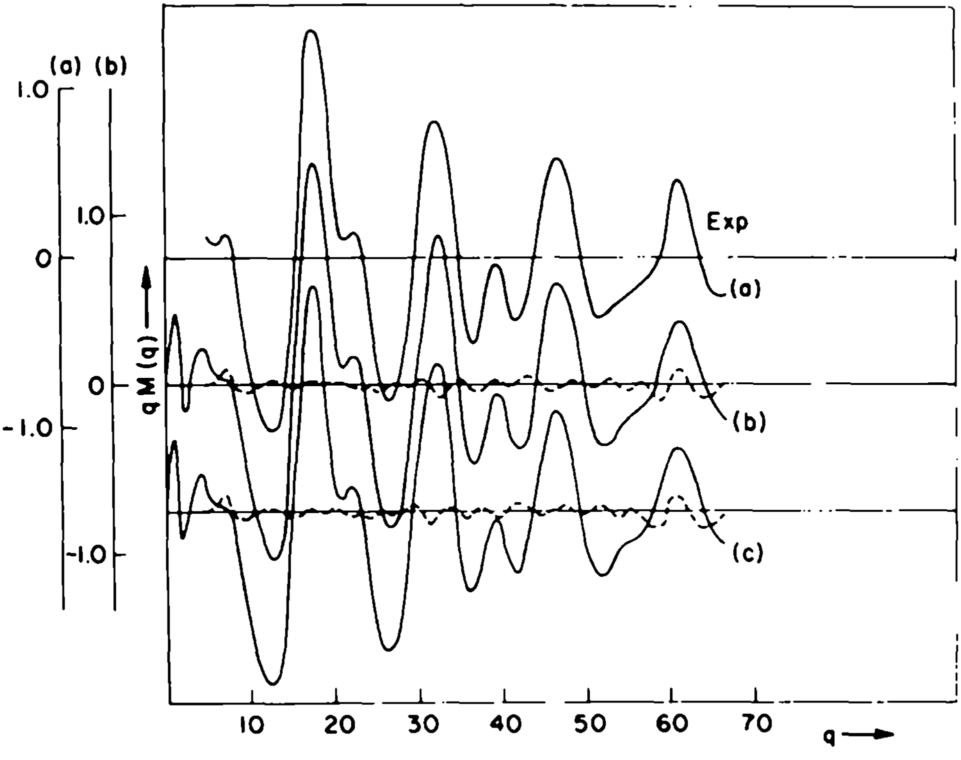


FIG. 2 The reduced experimental molecular intensity compared with calculated intensities. Curve (b) is that for the planar model (derived by least squares) allowing for no shrinkage, and (c) is the non-planar model (weighted average structure). The dashed lines indicate the deviations between the calculated and observed intensities.

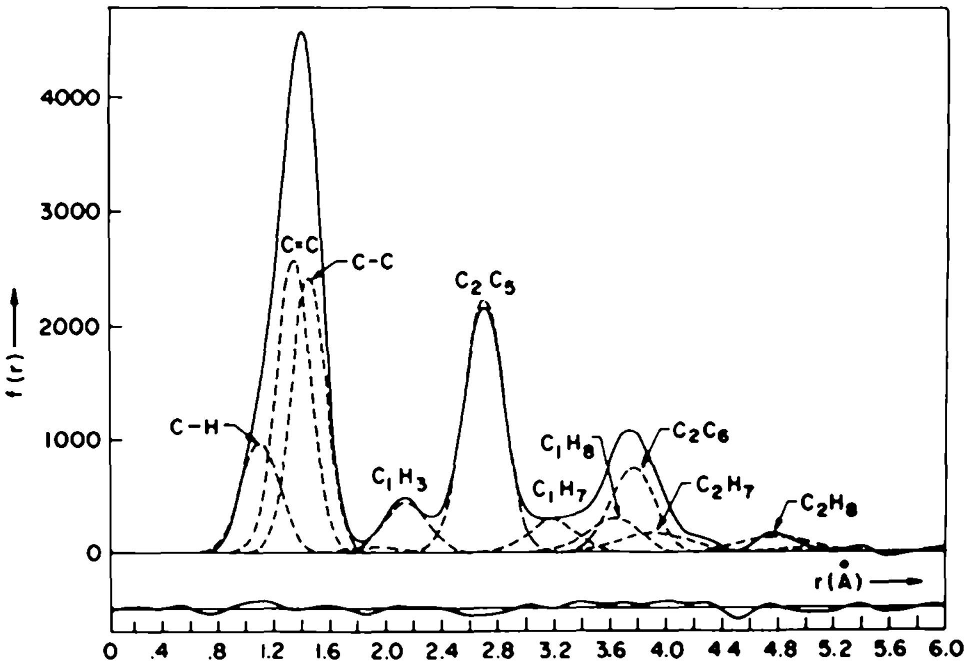


Fig. 3 The experimental radial distribution curve, resolved according to model (c) of Fig. 2. The undulating curve near the base line is the deviation between the experimental curve and the inverted theoretical intensity curve for that model.

DISCUSSION

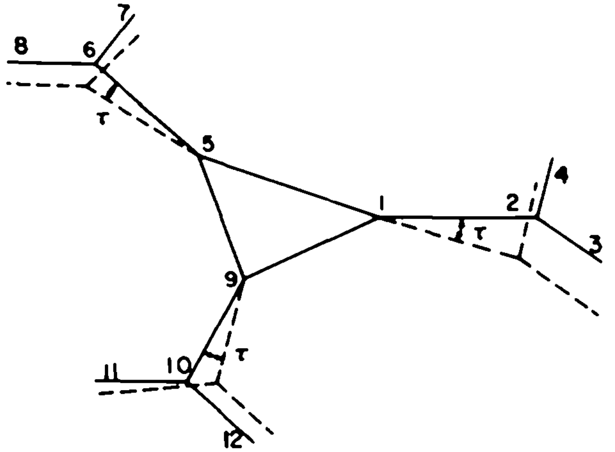
The molecule has a planar structure in which shrinkage is evident. The shrinkage effect precludes the possibility of experimentally establishing the molecule's planarity to less than an out-of-plane angle of 7·7°. However, the determination of interatomic distances is not greatly affected by this.

The observed bond lengths in TMCP (non-planar model, corrected for shrinkage) agree well with those predicted by Dewar and Gleicher,[4] who assumed localized bonds and an empirical relation between bond length and bond order. Their results for the monocyclic isomers of C_6H_6 are summarized in Table 3. Nevertheless, it is interesting to compare the experimental values with those in related molecules in order to check whether there is a bit more electronic delocalization in TMCP than in butadiene. Observed bond lengths in several related molecules are listed in Table 4.

Attention is called to the relative shortness of the carbon–carbon single bond (1·453 ± 0·020 Å) compared with that in cyclopropane.[17] The C=C distance (1·343 ± 0·020 Å) and the C—H bond length (1·108 ± 0·015) are essentially the same as in ethylene.[18] The shortness of the C—C bond relative to that in cyclopropane suggests that it is inappropriate to assume complete localization of bonding, to regard TMCP as a linear combination of ethylene and cyclopropane. A less naive view, which has some merit, is to treat TMCP as a ternary combination of butadienes. The single bond in TMCP is indeed shorter than the single bond in butadiene[19a] by 0·011 Å. This decrement, though somewhat less than the shortening (0·025 Å) of the

C—C bond in cyclopropane relative to that in ethane,[20] can be attributed to a similar effect operating in both systems.

Neither of the above descriptions adequately accounts for the observation that the carbon–carbon double bond in TMCP is longer than the double bond in the related molecules methylenecyclopropane[21] and Feist's acid (3-methylenecyclopropane-*trans*-1,2-dicarboxylic acid).[22] The shorter C=C length in the latter is similar to that in the cumulenes[23, 24] and is described as an sp–sp^2, σ bond.[25] The description of bonding given by Walsh[26] for cyclopropane, which has received theoretical support from Coulson,[27] postulates sp^2 hybridized carbon atoms to form the ring. The bonding, in methylenecyclopropane according to this description is illustrated in Fig. 5a. One of the sp^2 carbon atoms in the cyclopropane ring has been replaced by an sp carbon which results in a shortening of the double bond length. Concurrently there is a decrease in the carbon–carbon single bond lengths adjacent to the sp carbon relative to cyclopropane (i.e. by the replacement of an sp^2 orbital with a shorter sp orbital).



METHYLENE CYCLOPROPANE

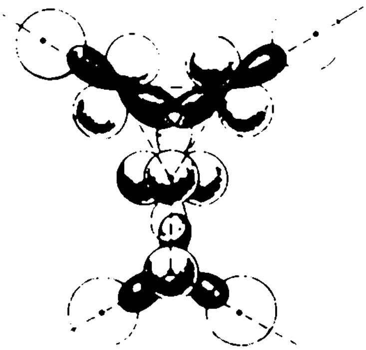


Fig. 5b is a similar description of the bonding in TMCP. Such a model explains the shortening of the C–C bond lengths relative to cyclopropane in terms of the shorter *sp* orbitals of TMCP relative to the sp^2 orbitals in cyclopropane. The lengthening of the C═C bonds in TMCP over that in methylenecyclopropane is rationalized in

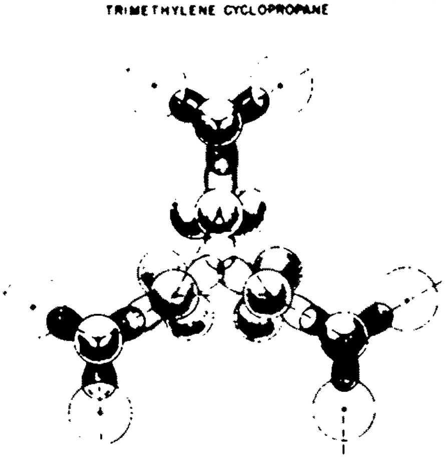


TABLE 1. REFINED GEOMETRIC PARAMETERS FOR TRIMETHYLENECYCLOPROPANE (IN Å)

	Weighted average model[a]	Planar model no shrinkage
C═C	1·343 ± 0·02	1·334 ± 0·02
C–C	1·453 ± 0·02	1·457 ± 0·02
C–H	1·108 ± 0·015	1·101 ± 0·015
<CCH	121·8° ± 2°	122·5° ± 2°

Interatomic Distances (in Å)

	r_{ij}[c]	l_{ij}	$r_{ij}(0)$[b]	$\delta_{ij}(0)$[b]	r_{ij}[c]	l_{ij}
$r_{C=C}$	1·343	0·069 ± 0·011	1·347		1·334	0·067 ± 0·011
r_{C-C}	1·453	0·065 ± 0·011	1·456		1·457	0·056 ± 0·011
$r_{C_2C_4}$	2·695	0·099 ± 0·002	2·698	0·009	2·695	0·099 ± 0·002
$r_{C_5C_6}$	3·758	0·111 ± 0·007	3·761	0·028	3·767	0·110 ± 0·007
r_{C-H}	1·108	0·088 ± 0·007			1·101	0·088 ± 0·007
$r_{C_1H_5}$	2·144	0·110 ± 0·009				0·110 ± 0·009
$r_{C_1H_7}$	3·186	0·12[d]				0·12[d]
$r_{C_1H_8}$	3·590	0·12[d]				0·12[d]
$r_{C_3H_7}$	3·947	0·2[d]				0·2[d]
$r_{C_3H_8}$	4·760	0·2[d]				0·2[d]
$r_{H_5H_6}$	1·883	0·12[d]				0·12[d]
$r_{H_6H_7}$	3·819	0·2[d]				0·2[d]
$r_{H_6H_8}$	5·032	0·2[d]				0·2[d]
$r_{H_5H_8}$	5·702	0·2[d]				0·2[d]

[a] Non-planar model required, due to shrinkage effect; $\tau = 7·7 \pm 4$

[b] Shrinkages calculated from $r_g(0)$ values.

[c] $r_g(1)$ values; harmonic oscillator approximation.

[d] l_{ij}'s constrained to the values indicated.

terms of some delocalization of the π electrons in the double bonds. A measure of the delocalization inherent in the three member ring can be ascertained from the observed differences between the C—C bond lengths in cyclopropane, ethylenimine, ethylene oxide and ethylene sulfide. It is less in the latter three compounds than in C_3H_6 because of ring orbital conjugation with the heteroatom orbitals; lower portion of Table 4.

EXPERIMENTAL

The sample of trimethylenecyclopropane (hereafter referred to as TMCP) was prepared as described in Ref. 1. Except during use, it was maintained at −78°. Its purity was checked mass spectrometrically. The sample was used as prepared. Sectored diffraction patterns were recorded with an r^3 sector using the new apparatus in the convergent mode.[6, 7] During the exposures, a pressure of about 5 mm was maintained by keeping the sample tube at −10°. Kodak Process Plates, 4 in × 5 in, were used. An MgO pattern was recorded for each voltage at each sample-plate distance to provide the calibrating scale factor.

Polymerization of the sample caused considerable difficulty. Although sets of plates were made for three magnifications covering the scattering angle $q = 3$ to $q = 143$ [$q = 40/\lambda \cdot \sin \theta/2$, where λ is the electron wavelength and θ is the diffraction angle], only one set showed no evidence of impurities as ascertained by mass spectral analysis following the electron diffraction run. This set covered the range $5 < q < 66$.

The plates were microphotometered on a modified Jarrell Ash microdensitometer fitted with a rotating plate holder.[8] Optical densities were converted to relative intensities by the method previously described.[9]

Data reduction

Reduction of the data and calculation of the experimental radial distribution function followed the usual procedures.[10] Trial and error adjustments of an assumed model was made until reasonable agreement was obtained between the experimental and theoretical radial distribution curves; then $M_{exp}(q)$, the experimental molecular intensity, as calculated from the best background and the experimental relative intensity, was fitted by least squares for the best set of molecular parameters. In calculating $M_{theor}(q)$, the x-ray form factors F_i and F_j were evaluated with the parametric equation of Cromer, Larson, and Waber,[11] while the incoherent scattering factors S_k were calculated from the expression proposed by Bonham and Ukaji.[12] The interatomic distances r_{ij} were expressed in terms of selected bond lengths and angles [Table 1, upper portion],[12] the parameters used in the refinement sequence; the resolution factor was also refined.

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TABLE 2. ERROR MATRIX

	$r_{C—C}$	$r_{O=C}$	τ	$r_{C—H}$	∠CCH	$l_{O=C}$	$l_{C—C}$	$l_{C_2C_3}$	$l_{C_2C_4}$	$l_{C\ H}$	$l_{C_1H_3}$
$r_{C—C}$	0·0098										
$r_{O=C}$	−0·0094	0·0098									
τ	−0·0079	0·0127	0·0345								
$r_{C—H}$	−0·0052	0·0060	0·0102	0·0062							
∠CCH	0·0104	−0·0110	−0·0143	−0·0082	0·0187						
$l_{O=C}$	−0·0104	0·0100	0·0079	0·0054	−0·0111	0·0114					
$l_{C—C}$	−0·0102	0·0104	0·0126	0·0060	−0·0115	0·0108	0·0113				
$l_{C_2C_3}$	−0·0007	0·0008	0·0016	0·0003	0·0006	0·0006	0·0010	0·0021			
$l_{C_2C_4}$	0·0027	−0·0020	0·0044	0·0016	0·0030	−0·0030	−0·0025	−0·0008	0·0067		
$l_{C\ H}$	−0·0063	0·0056	−0·0044	0·0023	−0·0061	0·0074	0·0059	−0·0005	−0·0022	0·0071	
$l_{C_1H_3}$	−0·0034	0·0034	0·0033	0·0022	−0·0047	0·0034	0·0034	0·0004	−0·0007	0·0011	0·0095

Units for distances in Å; for angles in radians

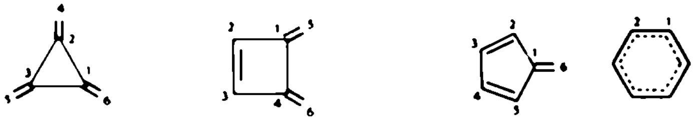
$$\sigma_{ij} = \mathrm{sgn}\,[([B]^{-1})_{ij}][|([B]^{-1})_{ij}|\chi_R/(n_q - n_p)]^{\frac{1}{2}}$$

where, χ_R is the sum of the squares of the residuals
n_q is the number of observations
n_p is the number of variable parameters

$[B] = [J]^t[w][J]$

and, $[J]$ is the Jacobian matrix
$[w]$ is the weight matrix

TABLE 3. MONOCYCLIC ISOMERS OF C$_6$H$_6$
Bond lengths calculated in Ref. 4 (in Å)



	PPP	SPO
1-2	1·463	1·469
2-4	1·349	1·346

	PPP	SPO	PPP	SPO
1-2	1·459	1·466	1·393	1·393
2 3	1·354	1·350		
3-4	1·446	1·454		
1 6	1·351	1·347		

PPP Pariser, Parr, Pople
SPO Split p-orbitals

TABLE 4. BOND LENGTHS IN RELATED MOLECULES

Molecule	C=C	C—C	Method	Ref.
TMCP	1·347	1·466	Calc (ave.)	(4)
Cyclopropane	—	1·509 ± 0·001$_5$	E.D.	(17)
Ethylene	1·3369 ± 0·001	—	E.D.	(18)
Butadiene	–	1·464 ± 0·003	M.W.	(19a)
	1·344	1·467	E.D.	(19b)
Ethane	—	1·5324 ± 0·001	E.D.	(20)
Methylenecyclopropane	1·312 ± 0·01	1·484 ± 0·01 (side) 1·535 ± 0·015 (unique)	E.D.	(21)
Feist's acid	1·317	1·494 (side) 1·545 (unique)	X-ray	(22)
Allene	1·312	-	E.D.	(23)
Butatriene	1·318	-	E.D.	(24)

	C—X	C—C		
Ethylenimine	1·488	1·480	M.W.	(28)
Ethylene oxide	1·435	1·470	M.W.	(29)
Ethylene sulphide	1·819	1·492	M.W.	(30)

E.D. Electron Diffraction
M.W Microwave

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