Bond Alternation in Tropone as Studied by Gas Electron Diffraction[1]

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Assuming a planar conformation with C_{2v} symmetry, and using the estimated mean amplitudes of vibration, the bond alternation in tropone was confirmed. The average C–C and C=C distances were determined by the least-squares method to be 1.454±0.010 and 1.362±0.013 Å respectively; moreover, two probable sets of the structure parameters were obtained. On the basis of conformational arguments regarding the structures of related compounds, the following set of the bond lengths was preferred: C–H, $1.09_8 \pm 0.01_6$ Å; C_1–O, $1.22_5 \pm 0.01_2$ Å; C_1–C_2, $1.44_5 \pm 0.01_2$ Å; C_2–C_3, $1.36_4 \pm 0.01_2$ Å; C_3–C_4, $1.46_2 \pm 0.01_2$ Å; and C_4–C_5, $1.34_2 \pm 0.01_8$ Å.

Since the geometrical configurations of nonbenzenoid aromatic seven-membered ring compounds have been the subject of much interest in conjunction with their aromaticity, a number of X-ray structure analyses have been undertaken regarding tropone derivatives,[2] tropolone[3] and its derivatives,[4] dicyanoheptafulvene[5] and its derivatives,[6] and many other related compounds. From the results of these studies, it may be said that the planarity[7] and bond alternation of the seven-membered rings of compounds, commonly classified as nonbenzenoid aromatics, have been established. As a natural consequence, tropone itself can also be expected to have a planar configuration with alternating bond lengths. This is in accordance with the theoretical consideration that the aromaticity of tropone originates from a significant contribution of a polar structure to the ground state.[8] Indirect but fairly conclusive experimental evidence for bond alternation was provided, for example, by the presence of the infrared bands assigned to the stretching vibrations of the C–C and C=C bonds.[9,10] In a previous electron diffraction study, one of the present authors and his coworkers were unable to draw a definite conclusion as to the bond alternation, instead, a regular heptagonal model was assumed.[11]

Many molecular orbital calculations were carried out[8,12–15] in order to interpret the ultraviolet absorption spectrum[8,12,16] and the dipole moment.[17,18] There still exist two alternative interpretations of the characteristic absorption bands of tropone; one was presented by Hosoya *et al.*[8a] and the other, by Weltin *et al.*[12] Because of a lack of accurate structural data, in most of the calculations the bond lengths were assumed at either the values determined by the previous electron-diffraction study or at those estimated from the observed bond lengths for olefins. Hosoya and Nagakura[8b] and Kunii and Kuroda[15] estimated the bond lengths on the basis of the resulting bond orders, but they had no experimental data by which to check their results. The former authors then remarked in their paper that a more precise determination of the lengths would provide an effective clue to settle the problem.[8b] Since it was expected that the current technique of electron diffraction by gases would yield more accurate bond lengths, we decided to reinvestigate this molecule.

After initiating this reinvestigation, we noticed that Bertelli and Andrews, Jr.,[19] had analysed the dipole

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[1] Presented at the International Symposium on Nonbenzenoid Aromatic Compounds, Sendai, Japan, 1970 (abbreviated by ISNA in this paper).

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[7] The planarity of the seven-membered rings is not unexceptional. If the 2 and/or 7 positions of a ring (Fig. 3) are substituted by atoms or groups bulkier than the hydrogen atom, the ring may deviate from a plane and take a boat form by steric interactions between the carbonyl oxygen and the substituents.[2e,4e,6a,6b]

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moments and NMR spectra of tropone and analogous compounds by the aid of CNDO/2 molecular-orbital calculations for two assumed models, a regular heptagonal ring and a planar ring built from bond lengths suitable for olefins.[20] As a result, they were led to the conclusion that the dipole moment and NMR data are consistent with the planar ring with alternating bond lengths. Furthermore, through several critical discussions of its aromaticity, they stated that tropone resembled a polyenone more closely than an aromatic system and could be best classified as the former. If accurate bond lengths can be determined, they will provide useful information for discussions along this line.

In carrying out the present study, our attention was directed mainly to obtaining experimental evidence for bond alternation and, if possible, bond lengths useful for discussing the properties of tropone. Making some plausible assumptions regarding the molecular symmetry and the parameter values, which are necessary to analyze the diffraction patterns of relatively complex molecules, we obtained two probable sets of structural parameters. Unfortunately, a unique result could not be obtained from the electron diffraction data alone. However, the bond alternation in tropone has unquestionably been verified.

Experimental

The sample of tropone was kindly provided by Professor Yoshio Kitahara of Tohoku University and was used without further purification. The diffraction photographs were taken with an apparatus equipped with an r^3-sector at the camera length of 124.47 mm.[21] The sample vapor was injected into the diffraction chamber by means of a high-temperature nozzle maintained at 108°C. The exposure time was 8 min, with a beam current of 0.15 μA. The wavelength of the beam (an accelerating voltage of about 52.9 kV) was determined by the use of the pattern of carbon disulfide.[22] Three plates were selected from among several plates and were microphotometered.

Data Processing and Structure Determination

The molecular intensity, $qM(q)$, was obtained from the observed total intensities[23] by determining the experimental background by means of the radial distribution curve and its Fourier inverse transformation. In the calculations of the radial distribution curves, the correction factors for non-nuclear scattering were introduced by Bonham and Bartell's method.[24] The other details of data processing have been described elsewhere.[25]

The determination of the molecular parameters was carried out by the least-squares method based upon the molecular intensity.[26] According to our conventional weighting scheme, the data were weighted down from $q=30$ to 21 and from $q=100$ to 130 in order to reduce the influence of uncertainties in the experimental molecular intensities at both small and large scattering angles. In general, accurate determination of interatomic distances are practically impossible for atom pairs which make relatively small contributions to the molecular intensity. Besides, the skeletal heptagonal ring of tropone consists of bonds which are only slightly different in length from one another. In such a case, the mean amplitudes and the differences between the bond lengths are strongly correlated if one wishes to determine all of them from the diffraction pattern by the least-squares method. After various preliminary least-squares treatments, it was found best for our present purpose to use reliable estimates of the mean amplitudes in order to fix some of the strongly correlated parameters and to determine the bond lengths more precisely. The following assumptions were made with respect to the geometrical configuration and mean amplitudes:

(1) Configuration. The molecule has a planar configuration, with C_{2v} symmetry. All the C–H bonds have the same length, and each of them bisects the CCC valence angle. The molecular configuration is, then, defined by the eight interatomic distances, the bonded C–H, C_1–O, C_1–C_2, C_2–C_3, C_3–C_4, C_4–C_5 and non-bonded $C_1\cdots C_3$, $C_1{:}{:}{:}C_4$ distances (see Fig. 3).

(2) Mean Amplitudes. The mean amplitude used were estimated from the spectroscopic data in the following way. By assuming an appropriate molecular configuration, the Urey-Bradley force constants were determined from the vibrational frequencies observed by Ikegami.[9] The mean amplitudes were then calculated at 373°K, the approximate temperature of the nozzle when the diffraction experiments were carried out. The calculation was limited to in-plane vibrations. The calculated mean amplitudes for the ring and the force constants are shown in Tables 1 and 2 respectively.

Table 1. Mean amplitudes used for the analyses (at $T=373$°K)

Pair	l (Å)	Pair	l (Å)
C_1—O	0.0413	$C_2{:}{:}{:}C_5$	0.0699
C_1—C_2	0.0470	$C_2{:}{:}{:}C_6$	0.0707
C_2—C_3	0.0441	$C_3\cdots C_5$	0.0575
C_3—C_4	0.0476	$C_3{:}{:}{:}C_6$	0.0708
C_4—C_5	0.0432	$O\cdots C_2$	0.0596
$C_1\cdots C_3$	0.0575	$O\cdots C_3$	0.0630
$C_1{:}{:}{:}C_4$	0.0692	$O{:}{:}{:}C_4$	0.0713
$C_2\cdots C_7$	0.0596	C—H	0.0771
$C_2\cdots C_4$	0.0588		

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TABLE 2. ADJUSTED VALUES OF THE FORCE CONSTANTS FOR TROPONE (IN mdyn/Å)

Bond	*K*	Angle	*H*	*F*
C=O	7.5	OCC	0.32	0.80
C_1–C_2	4.2	CCC[a]	0.33	0.37
C_2=C_3	6.0	HCC[a]	0.20	0.48
C_3–C_4	4.2			
C_4=C_5	6.6			
C–H	4.56			

a) The same values were assumed for all CCC and for all HCC force constants.

(3) Asymmetry Constants. The asymmetry constants were fixed at values of 30×10^{-7} and 127×10^{-7} Å^3 for the bonded distacnes in the skeleton and the C–H bond respectively, and were ignored for the non-bonded distances.[27]

In practical refinements, a strictly constrained least-squares method was not used; rather, unadjusted parameters at each step of calculation were fixed at values evaluated from the r_a distances obtained just before the step, without taking the shrinkage effect into account.[28]

The observed molecular intensities thus obtained for one arbitrarily selected plate are shown by dots in Fig. 1, while the corresponding radial distribution curve is depicted in Fig. 2, curve a. In the radial distribution curve, there are two complex peaks extending from 1.0 to 1.6 Å, and from 2.0 to 2.7 Å, with maxima at about 1.40 and 2.55 Å respectively. The former corresponds to the bonded atom pairs, and the latter, to the short non-bonded atom pairs. The peaks at about 3.15 and 3.55 Å represent the long non-bonded C:::C and the long non-bonded C:::O and C:::H distances respectively. The still longer distacnes, C:::O and C:::H, contribute to the peak beyond 4.0 Å.

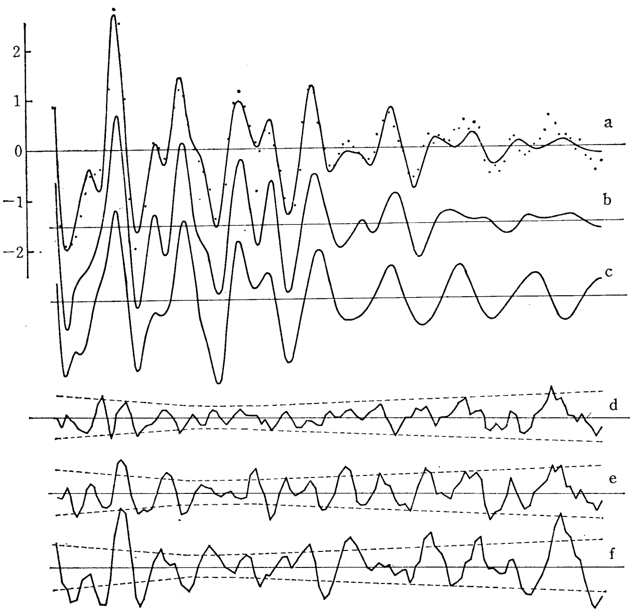

Fig. 1. The molecular intensity and difference curves.
dots: experimental, a: theoretical II, b: theoretical average (see text), c: theoretical non-alternating, d: Exp–a, e: Exp–b, f: Exp–c. The scale of the ordinate is the same for all the curves and is entered only for the experimental one. Broken lines indicate the limit of estimated uncertainties in the experimental intensities.

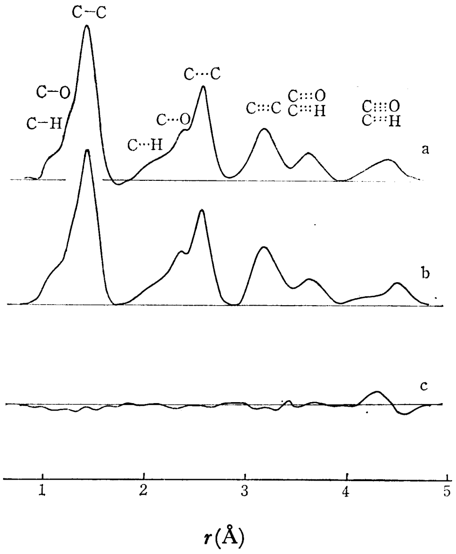

Fig. 2. The radial distribution curves.
a: experimental, b: theoretical II, c: difference a—b.

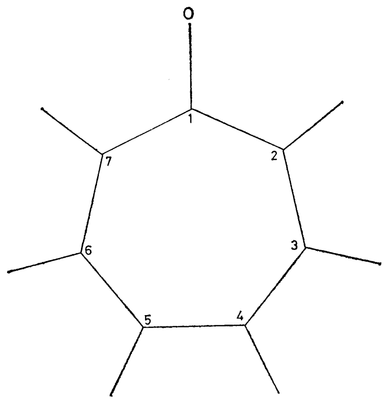

Fig. 3. The numbering of atoms.

Results

Non-equality of Bond Lengths and Average C–C and C=C Bond Lengths. The possibility of a configuration with non-alternating bond lengths was rejected after examining the results of least-squares fittings for various models. When a least-squares fitting was performed, for instance, with respect to the four independent parameters, the C=O, C–C, C···C, and C:::C, by fixing the mean amplitudes at the estimated values in Table 1 and the C–H distance at 1.092 Å, the structure parameters resulting from the data plotted in Fig. 1 were as follows: r_a(C=O), 1.284±0.016;

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Table 3. Average C–C and C=C, and other interatomic distances determined by the least-squares adjustment

Parameter	r_g	σ	limit of error[a]
C—C	1.454	0.002	0.010
C═C	1.362	0.003	0.013
C═O	1.231	0.005	0.016
$C_1\cdots C_3$	2.502	0.009	0.028
$C_1 ::: C_4$	3.197	0.013	0.035
C—H	1.098	assumed	

a) Described in the succeeding paragraph of the most probable structures.

r_a(C–C), 1.422±0.004; r_a(C⋯C), 2.507±0.029; r_a(C:::C), 3.109±0.044 Å, and the index of resolution, 0.55±0.03. The theoretical curve based upon these parameters and its differences from the experimental values are shown in Fig. 1c and f respectively. The disparities between the experimental and theoretical curves are far beyond the estimated uncertainties in the observed intensities, shown by broken lines in Fig. 1. The average C–C and C=C bond lengths were then determined by dividing bonds in the ring into two groups, a single bond C_1—C_2, C_3—C_4, *etc*, and a double bond, C_2—C_3, C_4—C_5 *etc*. The results of the least-squares refinement are shown in Table 3. In this table, each structure parameter was given by the average of the results obtained from the three sets of data, while the standard deviation, σ, was estimated by the equation, $\sigma = \langle\sigma\rangle/\sqrt{3}$, where $\langle\sigma\rangle$ is the average of the three standard deviations. The corresponding theoretical intensity curve and its differences from the experimental values are depicted in Fig. 1b and e respectively. The agreement between the theoretical curve and the experimental one was improved to some extent; the sum of square residuals was reduced by a factor of about 2, while the index of resolution increased to 0.82±0.04.

The Most Probable Parameters. Further least-squares refinements were carried out for models with different bond lengths. Since it was difficult to make the refinements converge by allowing the index of resolution and the eight independent distances to vary simultaneously, the index of resolution, the five bonded distances in the skeleton, the C–H distance, and each of the two non-bonded distances were adjusted iteratively so as to make a best-fit theoretical molecular intensity curve. By reference to the average C–C and C=C bond lengths, and also to the reported values for tropone derivatives in the crystalline state, a model with C_1–O=1.23, C_1–C_2=1.48, C_2–C_3=1.37, C_3–C_4=1.43, C_4–C_5=1.34, and C–H=1.10 Å, and others with bond lengths exchanged with respect to either one or both of the C_1–C_2 and C_3–C_4 and the C_2–C_3 and C_4–C_5 pair, were selected initially in order to search for the most probable structure. As a result, we found two sets of parameters which were equally probable and gave the same least-square residuals. Table 4 summarizes the results obtained by the least-squares refinements from the data for three plates. In what follows, these two sets of the parameters will be referred to as I and II.

The two sets of parameter values thus derived explain the experimental molecular intensities equally well, the indices of resolution and the standard deviations being substantially equal in both refinements. The agreement of the theoretical intensity curves for these models with the experimental one was much improved over the previous case, and the sum of the squared residuals was reduced to about one-half the value obtained for the model with the grouped C–C bond lengths. The two theoretical curves based upon the sets I and II differ from each other in some details. However, this cannot be used in discriminating a better model, since the magnitudes of the differences are within the range of random fluctuations, or the limit of uncertainty in the observed intensities. For example, the theoretical intensity curve calculated from the parameters of the set II and its difference curve are shown

Table 4. Results of the least-squares adjustments and their estimated limits of error (distances in Å, angles in degrees)[a]

Parameter	I			II		
	r_g[b]	σ[c]	Limit of error	r_g[b]	σ[c]	Limit of error
C—H	1.096	0.005	0.014	1.098	0.006	0.016
C_1—O	1.224	0.004	0.012	1.225	0.004	0.012
C_1—C_2	1.475	0.002	0.012	1.445	0.002	0.012
C_2—C_3	1.362	0.002	0.012	1.364	0.002	0.012
C_3—C_4	1.429	0.002	0.012	1.462	0.002	0.012
C_4—C_5	1.342	0.005	0.016	1.342	0.006	0.018
$C_1\cdots C_3$	2.560	0.006	0.019	2.590	0.007	0.022
$C_1 ::: C_4$	3.250	0.009	0.026	3.227	0.009	0.027
Index of resolution	0.92	0.01		0.88	0.01	
$\angle C_7C_1C_2$[d]	125			122		
$\angle C_1C_2C_3$	127.5			133		
$\angle C_2C_3C_4$	133			126		
$\angle C_3C_4C_5$	127			129.5		

a) Distances in Å, angles in degrees and the indices of resolution are dimensionless.

b) Calculated from the observed r_a distances and the mean amplitudes listed in Table 1.

c) σ does not include the systematic errors.

d) Calculated from the r_g distances for the best-fit structure.

in Fig. 1 a and d respectively. Curve b in Fig. 2 shows the theoretical curve based upon the set II parameters. The agreement with the observed curve is satisfactory except for the peaks in the region beyond 4.0 Å, which are associated with the longest non-bonded distances.

The limits of error quoted in Tables 3 and 4 include the random error, taken as 2.5 times the standard deviation, σ, and the systematic errors. The most significant systematic errors are the error in the scale factor, which was estimated to be 0.15% of the interatomic distance from the results of analysis for the diffraction patterns of the reference material, carbon disulfide, and the errors due to the probable uncertainties in the mean amplitudes and the ignoring of the shrinkage effects. The last two errors were not evaluated numerically, but were estimated roughly as follows.

It is generally known that calculated mean amplitudes are not very sensitive to variations in the force constants of the internal force field if they are only chosen to account a same extent for the observed vibrational frequencies. There is, therefore, little probability that the mean amplitudes for tropone deviate more than 5% from the calculated values listed in Table 1. Five percent of the mean amplitudes in our case amounts to 0.0025 Å for the bonded distances and 0.0030 Å for the short non-bonded distances. These deviations will influence the results, particularly similar distances such as the C_1–C_2 and C_3–C_4, and the C_2–C_3 and C_4–C_5 distances. It was reported by Karle that if the neighboring C–C bonds of benzene differed in length by $2a$ Å, as much as $a/3$ Å smaller mean amplitudes would result.[29] This estimate seems reasonable. If this estimate is applied to the present case, we get, in a very crude approximation, values of the errors due to the uncertainties in the mean amplitudes of 0.008 Å and 0.009 Å for the bonded and short non-bonded distances respectively. For the long non-bonded distances, the error was estimated to be 0.011 Å by assuming simply the uncertainties in their mean amplitudes to be 10%. Since the C–H distance could be determined almost independently of its mean amplitude, an error of this sort was not included.

The shrinkage effects for various molecules have been dealt with by many workers.[28] By examining these results, we assumed the magnitude of shrinkage to be 0.006 Å, a value which is almost the largest value found for ordinary molecules with no extremely low deformaiton frequencies. The uncertainties due to the ignoring of the shrinkage effect in the analyses do not exceed this value. Thus, this amount of uncertainty was included in the limits of error. In considering the limits of error thus estimated, it should be remarked that we can attach no great significance to the differences obtained between the C_1–C_2 and C_3–C_4 distances and between the C_2–C_3 and C_4–C_5 distances by Refinement II.

Discussion

Bertelli and Andrews[19] employed, in their CNDO/2 calculations, the standard bond lengths proposed by Pople and Gordon,[20], and after some critical discussion of the aromatic character of tropone they stated that, although there were no direct measurements available, tropone must have bond lengths within the range found for polyolefinic compounds. Roughly speaking, their prediction about the bond lengths coincides with the results of the present study.

Now we have two probable sets of structural parameters. Unfortunately, it is impossible to select a preferred model on the basis of the electron diffraction data alone. Therefore, some other information is needed to decide which structure is more favorable. Hosoya and Nagakura estimated the average C–C and C=C bond lengths to be 1.46 and 1.35 Å respectively, by grouping the data into single and double bonds and by using various empirical relationships among the bond orders, bond length, overlap integrals, and core resonance integrals.[30–32] Kunii and Kuroda[15] estimated the self-consistent bond lengths to be 1.45, 1.37, 1.43, and 1.37 Å for the respective consecutive C–C bonds, and 1.27 Å for the C=O bond by the use of another relationship.[33] The bond lengths given by Hosoya and Nagakura are in perfect agreement with the average distances determined by the present study and are close to the set II structure, while those reported by Kunii and Kuroda agree better with the set I structure except for the C=O distance. As for the C=O distance, the former authors assumed it to be 1.26 Å, while the latter authors estimated it to be 1.27 Å. These values are unacceptably longer than the observed values, 1.22 Å. All of the molecular orbital calculation[8b,15,19] carried out so far lead to very similar bond orders for the C_1–C_2 and C_3–C_4 bonds, resulting in a difference in length of only 0.02 Å or less. If the similarity of the bond orders is a unique solution to be drawn from the molecular-orbital calculations, set I might be ruled out. However, this cannot be stated definitely at present.

It may be instructive to compare the present results with the bond lengths in ethylene,[34] *cis*-2-butene,[35] 1,3-butadiene,[36] 1,3,5,7-cyclooctatetraene (COT),[37] and 1,3,5-cycloheptatriene (CHT).[38] The structures of these molecules are illustrated in Fig. 4. The definitions of the distances shown in Fig. 4 are not identical with one another. However, they will not be affected by more than a few thousandths of one angstrom

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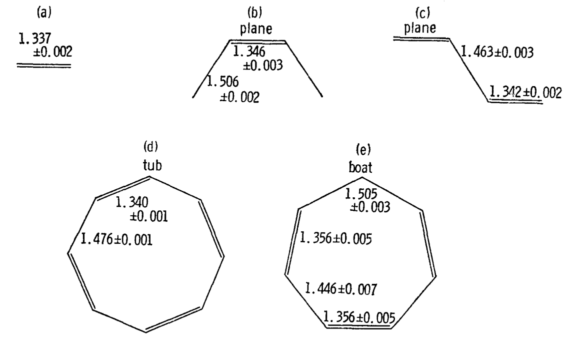

Fig. 4. Bond lengths for compounds related to tropone. (a): ethylene, r_g, Ref. 34, (b): *cis*-2-butene, r_a, Ref. 35, (c): 1,3-butadiene, $r_a{}^0$, Ref. 36, (d): 1,3,5,7-cyclooctatetraene (COT), r_a, Ref. 37, (e): 1,3,5-cycloheptatriene, r_a, Ref. 38. The $r_a{}^0$ is the distance r_a extrapolated to the absolute zero temperature.

when they are transformed into distances of the same physical significance. While no significant difference can be found between the C–C bonds of COT and butadiene, the C–C bond length in COT is longer than that in butadiene, and COT has a boat form.[37] The observed bond lengths in CHT except for the C_1–C_2 bond indicate a more conjugate-bond character than those in butadiene. Nevertheless, CHT takes a boat form with C=C–C valence angles of about 120° to relieve the strain in valence angles. Similar phenomena were observed[7] in the X-ray structure analyses of dibenzo[b, f]tropone,[2e] 1-isopropyl-8,8-dicyanoheptafulvene,[6a] and 1,6-dimethyl-8,8-dicyanoheptafulvene,[6a] all of which have $C_2C_3C_4C_5C_6$ frames very close to that in CHT. In such molecules which favor boat forms, however, the C_1–C_2 and C_1–C_7 bonds are usually longer than other single bonds in the same molecule. These facts imply that the conformations of such molecules are determined by a subtle compromise among various factors *e.g.*, π-electron delocalization, steric interaction, and strain in valence angles. When we compare our results with these facts, the set II structure seems to be more likely than the set I structure to have planar structure.

By considering additionally the fact that the vibrational spectra of tropone could be explained by using two kinds of force constants, 4.0 mdyn/Å for the longer bonds and 6.0 and 6.2 mdyn/Å for the shorter bonds, we are inclined to prefer, for the time being, the set II structure, where the bond lengths of the C_1–C_2 and C_3–C_4 bonds are about 1.45 Å, the C_2–C_3 and C_4–C_5 about 1.36 Å, and the C–O about 1.22 Å, and where the planarity is attained by π-electron delocalization.

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