An Electron Diffraction Investigation of Triphenylmethane

in the Gas Phase

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The molecular structure of triphenylmethane has been investigated by electron diffraction by the vapour. The molecule has C_3 symmetry and the molecular parameters for the phenyl groups are: C—C: 1.40_3 Å; C—H: 1.08_4 Å. The C—C distance from the central atom is 1.53 Å. The $\angle$ CCC at the central carbon is 112° and the angle of rotation of the phenyl groups $\varphi = 45°$. The angle φ is defined as zero when the ring plane normal lies in the plane determined by the three-fold axis and the central bond to the ring.

The electron diffraction investigation of the molecular structure of triphenylmethane in the gas phase has been carried out in order to compare the results with those obtained in a similar electron diffraction investigation of the triphenylmethyl free radical.[1] A comparison of angles and bond lengths around the central carbon atom and the rotation of the phenyl groups in the two compounds made it necessary to solve the triphenylmethane structure completely. An X-ray crystallographic investigation of triphenylmethane by Pascard-Billy [2] has been reported in progress but no structural information has yet been given. There are, however, reasons for believing that the angular distribution of the phenyl groups may be different in the free molecule from that in the crystalline state, as has been found for instance in the case of biphenyl.[3-5]

EXPERIMENTAL

Triphenylmethane was sublimed between 160°C and 190°C. Electrons of wavelength $\lambda = 0.06447$ Å were used in the experiment and diffraction pictures were recorded on photographic plates at two distances, approximately 19 cm and 49 cm from the point of scattering. The photometer curves were treated in the usual way.[6] Corrections for non-linearity of photographic blackening for a rotating sector with angular opening approximately proportional to s^3 and subtraction of a background were carried out in order to obtain the molecular intensity curves. The final intensity curve resulting from the curves obtained from the two scattering distances extends from $s = 1.25$ Å^{-1} to $s = 46$ Å^{-1} and is shown in Fig. 1. This curve contains the factor $Z_c^2(Z-F)_c^{-2}$ and corrections to the background deduced from a trial structure approximating the final structure.
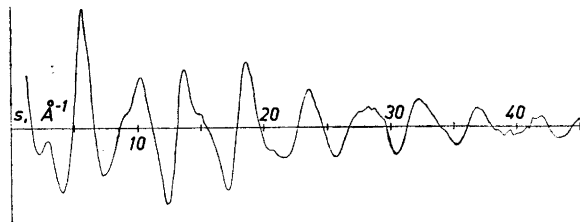
Fig. 1. Triphenylmethane intensity curve.

ANALYSIS OF THE RADIAL DISTRIBUTION CURVE

The experimental radial distribution curves were calculated from the observed intensity curve using three different values for k in the damping factor $\exp(-ks^2)$. The following values were used for k: 0, 0.0009, and 0.0036. The radial distribution curve with the heaviest damping is reproduced in Fig. 2. The envelope corresponding to the inner unobserved part of the intensity
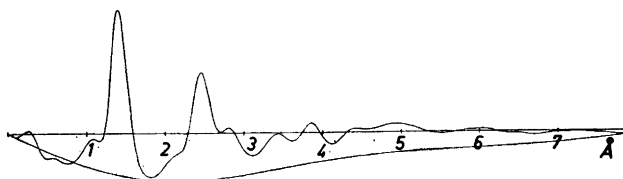

Fig. 2. Triphenylmethane radial distribution curve ($k = 0.0036$) with the envelope corresponding to the calculated inner unobserved part of the intensity curve.

curve is calculated on basis of the determined structure and is drawn in the same figure.

There are no indications that the molecule does not have a three-fold axis of symmetry and accordingly, the number of possible distances is reduced. If only C...C and C...H distances are taken into account, there are 107 different distances and they can all be expressed as functions of five parameters. As shown in Fig. 3 the parameters are the C(1)—C(2), C(2)—C(3) and C(3)—H(14) bond lengths, the angle γ at the central carbon atom C(1), and the angle φ which expresses the degree of rotation of the phenyl groups. The angle φ is equal to zero when the ring-plane normal lies in the plane determined by the threefold axis and the central bond to the ring. All distances within the benzene ring and between the benzene ring and the central carbon atom are independent of the two angular parameters. These are the most stable distances and their contribution dominates the intensity curve. All other distances depend on either γ or γ and φ in addition to the bond parameters. They are all very sensitive to thermal motions in the molecule and their contribution to the intensity curve is insignificant beyond $s = 15$ Å^{-1}.
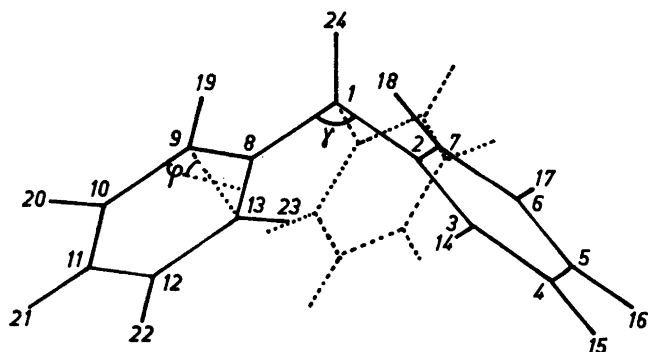
Fig. 3. Numbering of atoms in the triphenylmethane molecule.

The first parameters do not influence the position and shape of all maxima in the radial distribution curve (Fig. 2) to the same extent. Although the inner part of the distribution curve is more or less independent of the parameters γ and φ, these parameters do dominate the shape of the outer part of the curve. The maxima of the outer part of the curve contain a great number of distances and the position of the maxima cannot be determined as accurately as the maximum around 1.4 Å for example, and no single distance can be found which is responsible for the position of the peaks. Variations in the γ and φ parameters can cause pronounced changes, however. Therefore, some parts of the radial distribution curve have been used to determine the bond length parameters and other parts the angular parameters.

Fig. 4 shows a difference curve between the radial distribution curves of triphenylmethane and benzene [7] from $r = 0.8$ Å to $r = 3.0$ Å. The peak corresponding to the C(1)—C(2) bond is expected slightly above 1.5 Å and the next peak which is mainly determined by the C(1)...C(3) and C(2)...C(8) distances is expected between 2.5 and 2.6 Å.
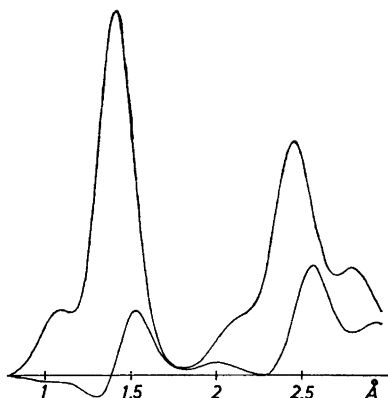

Fig. 4. Difference curve between the radial distribution curves of triphenylmethane and benzene together with the inner part of the distribution curve of triphenylmethane.

All interatomic distances were expressed as functions of the five parameters and theoretical radial distribution curves were calculated according to the formula:

$$\frac{\sigma_{theor.}(r)}{r} = \frac{1}{\sqrt{2\,\pi}} \sum_{dist.} \frac{n_{ij}Z_iZ_j}{r_{ij}{}^e\sqrt{u_{ij}{}^2 + 2k}} \, \exp\left[-\frac{(r_{ij}-r_{ij}{}^e)^2}{2u_{ij}{}^2 + 4k}\right]$$

where u_{ij} is the root-mean-square deviation from the equilibrium distance $r_{ij}{}^e$, n_{ij} number of times the distances occurs, and k the damping constant. The sum is taken over all C...C and C...H distances.

Deviations from the Gaussian shape of the C...H distances are not taken into account. The u_{ij} values have not been determined from the radial distribution curve. Those from benzene have been applied on the ring distances and the other ones have been estimated to give maxima of the appropriate height.

The outer part of the radial distribution curve ranging from $r = 3.5$ Å to $r = 7.5$ Å is reproduced in Fig. 5 with the theoretical distribution curves
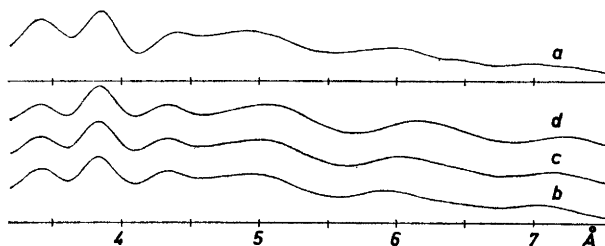
Fig. 5. The outer part of the radial distribution curve of triphenylmethane.
a: Experimental distribution curve. Theoretical distribution curves. b: $\varphi = 40°$; $\gamma = 111°$; c: $\varphi = 40°$; $\gamma = 113°$; d: $\varphi = 40°$; $\gamma = 115°$.

where the parameter φ is kept constant at 40° and γ has the values 111°, 113°, and 115°. There are small changes in the curve in the interval of r between 3.5 Å and 4.5 Å and the general appearance of the curve from r around 4.5 Å to 7.5 Å remains the same as γ increases. The postions of the three maxima at
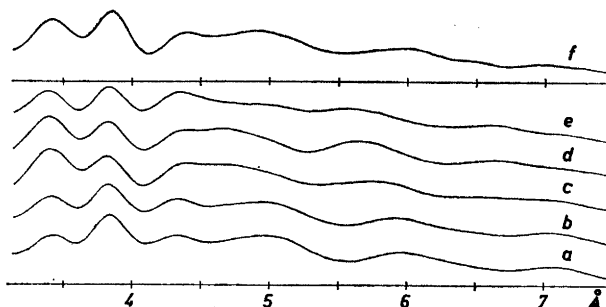

Fig. 6. The outer part of the radial distribution curve of triphenylmethane. Theoretical distribution curves. a: $\varphi = 70°$; $\gamma = 111°$; b: $\varphi = 60°$; $\gamma = 111°$; c: $\varphi = 50°$; $\gamma = 111°$; d: $\varphi = 40°$; $\gamma = 111°$; e: $\varphi = 37°$; $\gamma = 111°$. f: Experimental distribution curve.
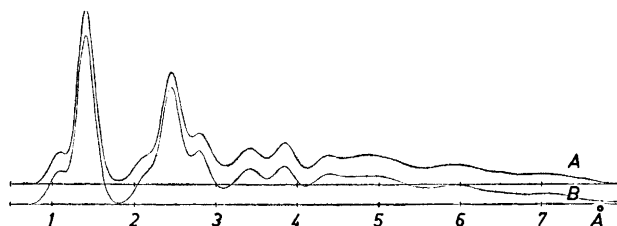
Fig. 7. Experimental (A) and theoretical (B) radial distribution curves of triphenyl-
methane.

about 5 Å, 6 Å, and 7 Å are continuously shifted towards higher r values
with increasing γ. Theoretical distribution curves keeping γ constant and vary-
ing φ are shown in Fig. 6. Here γ is equal to 111° and φ has the values 37°,
40°, 50°, 60°, and 70°. The experimental curve is again reproduced for compari-
son. The relative heights of the maxima below 4.5 Å are altered appreciably
but less pronounced changes of their positions occur. There are greater changes
in the outer part of these curves than in the curves above with constant φ.
This is mainly due to the larger intervals in the parameter values here. The
three maxima of this part of the curve remain but their positions are shifted
towards lower r-values as φ increases.

RESULTS AND DISCUSSION

The bond distances were determined mostly from the inner part of the
radial distribution curve, $r < 3.0$ Å, and the following parameters were deter-
mined: C(1)—C(2): 1.53 Å; C(2)—C(3): 1.40_3 Å; C—H: 1.08_4 Å. For the angular
parameters determined from the outer part of the distribution curve, $r > 3.0$
Å, the following values were found: $\gamma = 112°$ and $\varphi = 45°$.

All C...C and C...H distances calculated using the above parameter values
are listed in Table 1, and the theoretical radial distribution curve calculated
from these distances is reproduced in Fig. 7 with the experimental curve.

A theoretical intensity curve was calculated from the same distances and
the calculated and observed intensity curves are shown in Fig. 8. The accuracy

Fig. 8. Experimental (A) and theoretical (B) intensity curves of triphenylmethane.

Table 1. Interatomic distances and u values of triphenylmethane calculated from the molecular parameters C(1)—C(2) = 1.53 Å, C(2)—C(3) = 1.53 Å, C(3)—C(3) = 1.403 Å, C—H = 1.084 Å, φ = 45° and γ = 112°. Numbering of atoms as in Fig. 3.

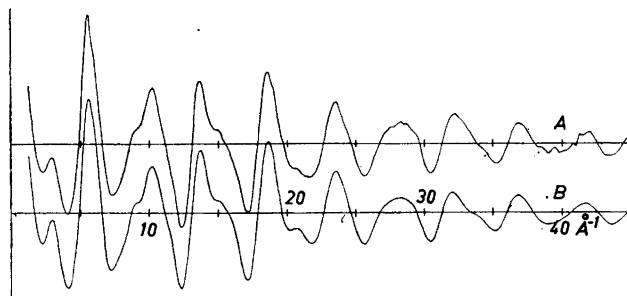| Distance	r(Å)	u	Distance	r(Å)	u	Distance	r(Å)	u	Distance	r(Å)	u
C(1)—C(2)	1.53	0.05	C(3)—C(12)	4.29	0.20	C(9)—H(14)	2.92	0.20	C(5)—H(23)	5.13	0.20
C(1)—C(3)	2.54	0.06	C(3)—C(13)	3.29	0.20	C(9)—H(15)	5.39	0.20	C(6)—C(8)	4.95	0.20
C(1)—C(4)	3.83	0.07	C(3)—H(14)	1.08_4	0.07	C(9)—H(16)	6.98	0.20	C(6)—C(9)	5.93	0.20
C(1)—C(5)	4.34	0.08	C(3)—H(19)	3.87	0.20	C(9)—H(17)	6.92	0.20	C(6)—C(10)	7.08	0.20
C(1)—H(14)	2.74	0.11	C(3)—H(20)	5.33	0.20	C(9)—H(18)	5.24	0.20	C(6)—C(11)	7.39	0.20
C(1)—H(15)	4.70	0.13	C(3)—H(21)	5.77	0.20	C(10)—H(14)	3.64	0.20	C(6)—C(12)	6.63	0.20
C(1)—H(16)	5.42	0.15	C(3)—H(22)	4.98	0.20	C(10)—H(15)	6.03	0.20	C(6)—C(13)	5.37	0.20
C(2)—C(3)	1.40_3	0.05	C(3)—H(23)	3.37	0.20	C(10)—H(16)	7.92	0.20	C(6)—H(19)	6.00	0.20
C(2)—C(4)	2.43	0.06	C(4)—C(8)	4.23	0.20	C(10)—H(17)	8.12	0.20	C(6)—H(20)	7.91	0.20
C(2)—C(5)	2.81	0.06	C(4)—C(9)	4.95	0.20	C(10)—H(18)	6.54	0.20	C(6)—H(21)	8.39	0.20
C(2)—C(8)	2.54	0.10	C(4)—C(10)	5.79	0.20	C(11)—H(14)	3.92	0.20	C(6)—H(22)	7.18	0.20
C(2)—C(9)	3.53	0.20	C(4)—C(11)	6.00	0.20	C(11)—H(15)	6.17	0.20	C(6)—H(23)	4.98	0.20
C(2)—C(10)	4.72	0.20	C(4)—C(12)	5.43	0.20	C(11)—H(17)	8.42	0.20	C(7)—C(8)	3.82	0.20
C(2)—C(11)	5.11	0.12	C(4)—C(13)	4.52	0.20	C(11)—H(18)	6.94	0.20	C(7)—C(9)	4.85	0.20
C(2)—C(12)	4.48	0.20	C(4)—H(19)	5.17	0.20	C(12)—H(14)	3.58	0.20	C(7)—C(10)	6.09	0.20
C(2)—C(13)	3.20	0.20	C(4)—H(20)	6.54	0.20	C(12)—H(15)	5.69	0.20	C(7)—C(11)	6.46	0.20
C(2)—H(14)	2.16	0.09	C(4)—H(21)	6.87	0.20	C(12)—H(16)	7.41	0.20	C(7)—C(12)	5.73	0.20
C(2)—H(15)	3.41	0.10	C(4)—H(22)	5.97	0.20	C(12)—H(17)	7.61	0.20	C(7)—C(13)	4.39	0.20
C(2)—H(16)	3.89	0.10	C(4)—H(23)	4.42	0.20	C(12)—H(18)	6.19	0.20	C(7)—H(19)	4.92	0.20
C(2)—H(19)	3.70	0.20	C(5)—C(9)	5.97	0.20	C(13)—H(14)	2.85	0.20	C(7)—H(20)	6.95	0.20
C(2)—H(20)	5.58	0.20	C(5)—C(10)	6.96	0.20	C(13)—H(15)	5.01	0.20	C(7)—H(21)	7.52	0.20
C(2)—H(21)	6.16	0.20	C(5)—C(11)	7.19	0.15	C(13)—H(16)	6.41	0.20	C(7)—H(22)	6.38	0.20
C(2)—H(22)	5.22	0.20	C(5)—C(12)	6.50	0.20	C(13)—H(17)	6.33	0.20	C(7)—H(23)	4.07	0.20
C(2)—H(23)	3.14	0.20	C(5)—C(13)	5.42	0.20	C(13)—H(18)	4.80	0.20	C(8)—H(14)	2.44	0.20
C(3)—C(8)	2.84	0.20	C(5)—H(19)	6.10	0.20	H(14)—H(15)	2.49	0.32	C(8)—H(15)	4.84	0.20
C(3)—C(9)	3.59	0.20	C(5)—H(20)	7.74	0.20	H(14)—H(16)	4.31	0.32	C(8)—H(17)	5.92	0.20
C(3)—C(10)	4.53	0.20	C(5)—H(21)	8.11	0.20	H(14)—H(17)	4.97	0.32	C(8)—H(18)	4.19	0.20
C(3)—C(11)	4.82	0.20	C(5)—H(22)	7.00	0.20						

of the bond length determination is not easily specified in electron diffraction. The ring parameters are not significantly different from those found in benzene [6] although small variations within the ring would not be detectable in a molecule of this size. The central carbon-carbon distance probably does not have an error exceeding 0.02 Å and the limits of error for γ and φ are 2° and 5°, respectively. Attempts have been made to fit a less symmetrical structure to the radial distribution curve. This is possible to some extent but the contribution from the ring to ring distances must be damped much more heavily than in the proposed structure wich appears rather unlikely.

The determined structure is not far from what is expected. The carbon-carbon distance from the central atom is usually somewhat shorter in molecules with similar hybridisation on the carbon atoms. The degree of rotation of the phenyl groups does not seem to be determined by hydrogen-hydrogen or hydrogen-carbon approach in adjacent rings but by the carbon-carbon distances. The H(14)...H(23) is 3.21 Å and the C(3)...H(23) distance is 3.27 Å, on the other hand C(3)...C(13) equals 3.29 Å. The distance from H(24) to H(18) is 2.57 Å which is reasonable.

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