An Electron Diffraction Investigation of the Free Radical Triphenylmethyl in the Gas Phase

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An electron diffraction investigation of the triphenylmethyl free radical in the gas phase has been carried out on evaporated hexaphenylethane. The following molecular parameters have been determined: The C—C distance from the central carbon atom 1.48 Å, the C—C distance in the rings 1.395 Å, C—H equal to 1.11 Å, $\gamma = 116—118°$ and $\varphi = 40—45°$. The angle φ is defined as zero when the ring-plane normal lies in the plane determined by the threefold axis and the central bond to the ring. Owing to the thermal movements the central angle γ and the angle of rotation φ of the phenyl groups cannot be determined very accurately. The significance of the value of the central angle and the unexpected lengthening of the C—H bond is discussed.

No complete structure determinations of organic free radicals have been reported so far. In this laboratory, X-ray crystallographic studies on free radicals which are stable in the solid phase and electron diffraction studies on gaseous radicals are in progress. Even with radicals having a half-life of fractions of a second, the latter method would be expected to be very powerful. Besides the investigation reported here, a three-dimensional X-ray crystallographic investigation of tri-p-nitrophenylmethyl [1] is in its last stage of refinement at this laboratory.

As shown by Gomberg [2] in his classical experiment on hexaphenylethane, partial dissociation into triphenylmethyl radicals already occurs in solutions at room temperature. Ziegler and Ewald [3] measured the heat of dissociation to be approximately 11 kcal/mole which is not very different from the heat of dissociation of N_2O_4.

In order to compare the molecular parameters in triphenylmethyl with those of similar compounds, an electron diffraction investigation of triphenylmethane [4] was carried out simultaneously, and the phenyl group parameters were compared with those of benzene. [5]

EXPERIMENTAL

Hexaphenylethane was prepared using triphenylchloromethane and zinc in a Wurtz's synthesis. As recommended by Gomberg [6] a zinc rod was kept in a solution of triphenylchloromethane in acetone in order to obtain a purer compound. Electron diffraction pictures were taken under various experimental conditions. Some were taken at temperatures giving vapour pressure just high enough to obtain diffraction patterns, others were taken of vapour evaporating from the melting solid. All photographs were treated separately and the radial distribution curves examined independently in case the diffracting vapour was composed of a mixture of triphenylmethyl and hexaphenylethane with the composition dependent on temperature or contained other compounds formed during melting. As melting proceeded in the sample the vapour pressure remained constant but dropped to a negligible value when the sample melted completely. The compound formed by melting hexaphenylethane did not have a vapour pressure high enough to give electron diffraction patterns. The individual patterns did not indicate differences between one curve and another and the final radial distribution curve was calculated from an average of all exposures. The temperatures in the oven ranged from slightly below 100°C up to approximately 145°C.

The wavelength of the electrons was 0.06447 Å and diffraction photographs were taken at two distances from point of scattering to photographic plate — approximately 19 cm and 49 cm. The photometer curves of the plates were treated in the usual way.[7] Corrections for rotating sector with angular opening approximately proportional to s^3 were carried out and the background was subtracted to obtain the molecular intensity curve.

The intensity curve obtained from the average of all exposures at the two distances is reproduced in Fig. 1 and extends from $s = 1.25$ Å^{-1} to $s = 45$ Å^{-1}.
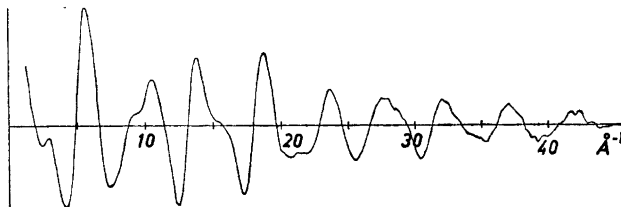

Fig. 1. Triphenylmethyl experimental intensity curve.

The subtracted background was adjusted as the structure determination proceeded and the intensity curve was multiplied by the factor $Z_c^2 (Z-F)_c^{-2}$ to obtain Gaussian shaped carbon-carbon peaks in the radial distribution curve.

ANALYSIS OF THE RADIAL DISTRIBUTION CURVE

Radial distribution curves were calculated by applying the following three values of k: 0, 0.0009, and 0.0036 in the damping expression $\exp(-ks^2)$. The distribution curves with k equal to 0.0009 and 0.0036 were mainly used in
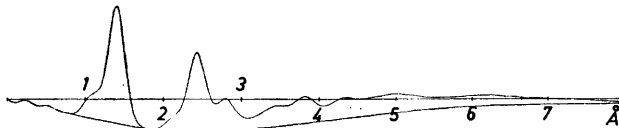

Fig. 2. Triphenylmethyl experimental radial distribution curve ($k = 0.0036$) and calculated envelope corresponding to the inner unobserved part of the intensity curve.

the analysis. The latter is reproduced in Fig. 2. The curve corresponding to the inner unobserved part of the intensity pattern was calculated from the proposed structure and is shown in the same figure.

Although nothing could be said for certain about the symmetry of the triphenylmethyl radical, the analysis of the radial distribution curve was carried out assuming C_3 molecular symmetry. Five independent parameters remain to determine the structure as is also the case for triphenylmethane. In a molecule of this size, deviations from a regular hexagonal configuration for the phenyl groups cannot be expected to be detected. The five independent molecular parameters are shown in Fig. 3. They are the three bond lengths C(1)—C(2)
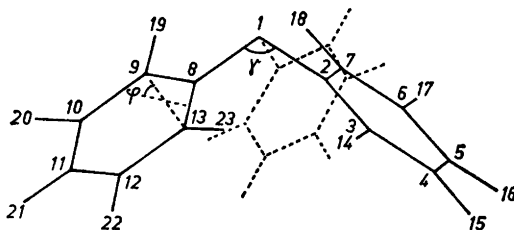

Fig. 3. Numbering of atoms in the triphenylmethyl radical.

from the central carbon atom, C(2)—C(3) in the ring, C—H, and the two angular parameters, the $\angle$C(2)C(1)C(8), called γ, and the angle φ which determines the degree of rotation of the phenyl groups about the C(1)—C(2)—C(5) axis. φ is defined as zero when the ring-plane normal lies in the plane determined by the threefold axis and the central bond to the ring. All interatomic distances were calculated as functions of these parameters. Theoretical radial distribution curves were calculated using the formula,

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

where u_{ij} is the root-mean-square deviation from the equilibrium distances r_{ij}^{e}, k the constant in the damping factor and n_{ij} the number of times a distance occurs. The summation is carried out over all C...C and C...H distances.

As in the case of triphenylmethane, variations in the bond length parameters will determine the positions and shapes of the maxima in the radial
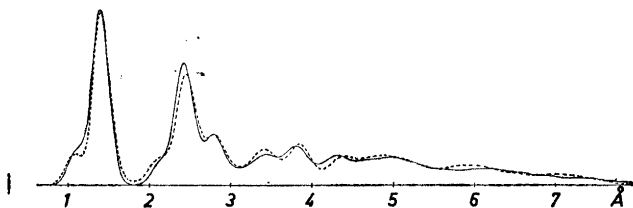

Fig. 4. Experimental radial distribution curve of triphenylmethyl (————) and triphenylmethane (------).

distribution curve for r less than 2.5—3 Å. The C(2)—C(8) distance will cause small changes, however, in the 2.5 Å region depending on γ. The accuracy of the bond length parameters determined from the inner part of the radial distribution curve cannot be improved by analysing the outer part. Many distances contribute to each maximum in the outer region and the positions cannot be determined accurately due to the large radius of curvature. In Fig. 4 the radial distribution curves of triphenylmethyl (solid curve) and triphenylmethane (broken line) are reproduced. A comparison of the two curves shows that most of the parameters must be different in the two compounds. The inner part of the distribution curve of triphenylmethyl ($r < 3$ Å) is shown in Fig. 5, and the difference curves between triphenylmethyl and benzene (broken line) are reproduced in the same figure. Both of the difference curves indicate significant differences in some of the bond length parameters. A smaller C(1)—C(2) bond length in triphenylmethyl than in triphenylmethane could be expected. The difference curves cannot be explained, however, unless either the C(2)—C(3) bond is shortened or the C(3)—H(14) bond lengthened or both. In Fig. 6 are shown calculated distribution curves based on the values, C(1)—C(2) = 1.48 Å, C(2)—C(3) = 1.395 Å and C(3)—H(14) = 1.084, 1.09, 1.10, and 1.11 Å. The Gaussian peaks (dotted line), their sum (solid line) and the experimental
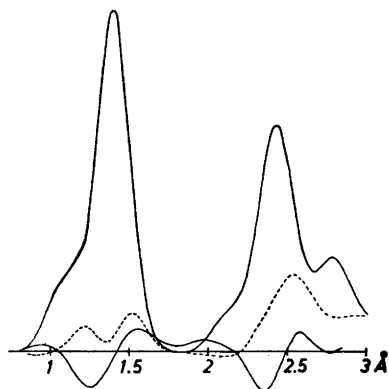

Fig. 5. Difference curves between triphenylmethyl and benzene (------) and triphenylmethane and triphenylmethyl together with the inner part of the distribution curve of triphenylmethyl.
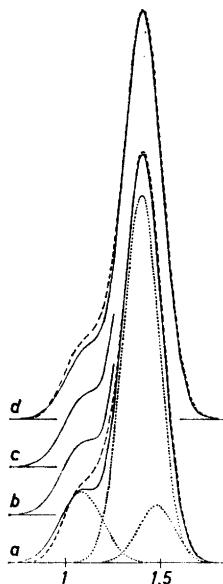
Fig. 6. Calculated first maximum of triphenylmethyl.   C(1)—C(2) = 1.48Å, C(2)—C(3) = 1.395 Å and C—H equal to a: 1.084 Å, b: 1.09 Å, c: 1.10 Å and d: 1.11 Å.
......Gaussian peaks: ------ experimental curve.

curve (broken line) are reproduced in the figure. The shape of the experimental curve in the region of overlap between the C—H and C—C distances can only be obtained by increasing the C—H bond distances. Variations in the C—C and C—H distances in the ring have not been taken into account in this investigation. The following values for the bond length parameters were determined from the inner part of the radial distribution curve ($r < 3$ Å): C(1)—C(2) = 1.395 Å; C(2)—C(3) = 1.48 Å and C(3)—H(14) = 1.11 Å.

If the difference between the two experimental radial distribution curves of triphenylmethane and triphenylmethyl is compared with the difference between the two theoretical distribution curves in the region $r < 3$ Å, good agreement is obtained as shown in Fig. 7. In calculating the radial distribu-
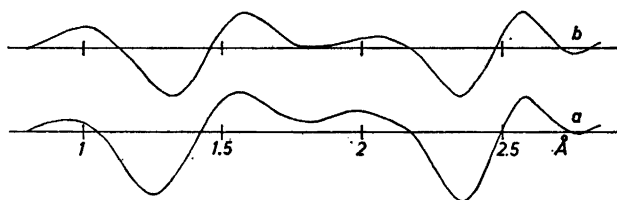

Fig. 7. Difference between the two experimental (a) and the two theoretical (b) radial distribution curves of triphenylmethane and triphenylmethyl.

tion curve all the carbon-carbon and carbon-hydrogen distances are included and the u values (the root-mean-square deviation from the equilibrium distance) are assumed to be the same as in triphenylmethane for all distances which are independent of the angular parameters. The angular parameters γ and φ were determined from the outer part ($r > 3$ Å) of the radial distribution curve. The two maxima at approximately 6 Å and 7 Å are less pronounced (Fig. 4) in the case of triphenylmethyl than in triphenylmethane indicating a heavier damping of the ring to ring distances in the radical. It can be seen from the same figure that the two maxima around 5 Å and 6 Å occur at larger r values in triphenylmethyl which can only be so if the angle γ is greater than the 112° value found in triphenylmethane.
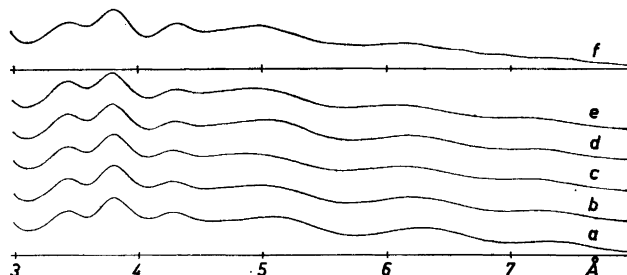

Fig. 8. The outer part of the triphenylmethyl radial distribution curve calculated for $\varphi = 45°$ and γ equal to a: 120°, b: 118°, c: 116°; $\varphi = 40°$ and γ equal to d: 118°, e: 116°, f: experimental $\sigma(r)/r$.

In Fig. 8 theoretical radial distribution curves are reproduced for the interval $r = 3$ Å to $r = 8$ Å. Curves a, b and c were calculated for parameter values $\varphi = 40°$ and $\gamma = 120°$, 118°, and 116°, respectively. Curves d and e were calculated for the values $\varphi = 45°$ and $\gamma = 118°$ and 116°; f is the experimental curve. The curves show that the parameter values cannot be determined very accurately although a central angle of $\gamma = 120°$ can be ruled out. If γ were equal to 120° the distances are concentrated in three groups resulting in the three outer maxima. The contribution of the distances must be much more damped to fit the experimental curve. Also the maxima occur at too large r values.

The greater uncertainty in determining the angular parameters γ and φ in triphenylmethyl than in triphenylmethane could be expected. The greater thermal movements of the phenyl groups in the free radical will make the φ and γ determination less accurate. Distribution curves calculated on a less symmetric molecule having a different φ parameter for each ring can be fitted to the experimental curve if the contributions of the distances are damped heavily enough.

The conclusion of the analysis of the outer part of the radial distribution curve is uncertain. A best fit to the experimental curve is obtained with the parameters, $\varphi = 40-45°$ and $\gamma = 116-118°$.

In Fig. 9 the experimental and theoretical radial distribution curves are reproduced. The molecular parameters used for the theoretical curve are:
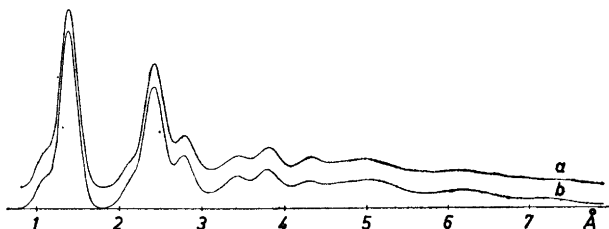

Fig. 9. Triphenylmethyl experimental (a) and theoretical (b) radial distribution curves. Theoretical curve molecular parameters: a: 1.48 Å, b: 1.395 Å, c: 1.11 Å, $\varphi = 45°$ and $\gamma = 118°$.

$C(1)-C(2) = 1.48$ Å, $C(2)-C(3) = 1.395$ Å, $C(3)-H(14) = 1.11$ Å, $\gamma = 118°$ and $\varphi = 45°$. The intensity curve calculated for same parameter values is shown in Fig. 10 with the experimental intensity curve. All carbon-carbon and carbon-hydrogen distances are included in the calculated curves. The interatomic distances calculated from the determined parameters are listed in Table 1.

DISCUSSION

The molecular parameters are not very different from what is expected, except for the large carbon-hydrogen distance. Although an evaluation of errors cannot be easily carried out, a comparison with triphenylmethane does give some indication of the relative accuracy of the bond length parameters.

Table 1. Triphenylmethyl interatomic distances and u-values calculated from the molecular parameters C(1)–C(2) = 1.395 Å, C–H = 1.11 Å, φ = 45° and γ = 118°. 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)	1.48	0.05	C(3) — C(12)	4.41	0.29	C(5) — H(23)	4.86	0.32	C(9) — H(14)	3.21	0.32
C(1) — C(3)	2.49	0.06	C(3) — C(13)	3.34	0.29	C(6) — C(8)	4.91	0.25	C(9) — H(15)	5.71	0.32
C(1) — C(4)	3.77	0.07	C(3) — H(14)	1.11	0.07	C(6) — C(9)	6.03	0.30	C(9) — H(16)	7.22	0.32
C(1) — C(5)	4.27	0.08	C(3) — H(19)	4.12	0.32	C(6) — C(10)	7.18	0.32	C(9) — H(17)	7.02	0.32
C(1) — H(14)	2.71	0.11	C(3) — H(20)	5.65	0.32	C(6) — C(11)	7.39	0.32	C(9) — H(18)	5.20	0.32
C(1) — H(15)	4.66	0.13	C(3) — H(21)	6.03	0.32	C(6) — C(12)	6.51	0.32	C(10) — H(14)	3.98	0.32
C(1) — H(16)	5.38	0.15	C(3) — H(22)	5.08	0.32	C(6) — C(13)	5.20	0.29	C(10) — H(15)	6.44	0.32
C(2) — C(3)	1.39_5	0.05	C(3) — H(23)	3.29	0.32	C(6) — H(19)	6.19	0.32	C(10) — H(16)	8.19	0.32
C(2) — C(4)	2.42	0.06	C(4) — C(8)	4.32	0.25	C(6) — H(20)	8.10	0.32	C(10) — H(17)	8.20	0.32
C(2) — C(5)	2.79	0.06	C(4) — C(9)	5.20	0.29	C(6) — H(21)	8.43	0.32	C(10) — H(18)	6.46	0.32
C(2) — C(8)	2.54	0.18	C(4) — C(10)	6.10	0.32	C(6) — H(22)	7.00	0.32	C(11) — H(14)	4.25	0.32
C(2) — C(9)	3.61	0.25	C(4) — C(11)	6.24	0.32	C(6) — H(23)	4.65	0.32	C(11) — H(15)	6.52	0.32
C(2) — C(10)	4.80	0.25	C(4) — C(12)	5.54	0.30	C(7) — C(8)	3.76	0.25	C(11) — H(17)	8.40	0.32
C(2) — C(11)	5.13	0.20	C(4) — C(13)	4.53	0.29	C(7) — C(9)	4.89	0.29	C(11) — H(18)	6.79	0.32
C(2) — C(12)	4.44	0.25	C(4) — H(19)	5.47	0.32	C(7) — C(10)	6.11	0.32	C(12) — H(14)	3.84	0.32
C(2) — C(13)	3.13	0.25	C(4) — H(20)	6.94	0.32	C(7) — C(11)	6.40	0.32	C(12) — H(15)	5.90	0.32
C(2) — H(14)	2.17	0.09	C(4) — H(21)	7.17	0.32	C(7) — C(12)	5.58	0.30	C(12) — H(16)	7.44	0.32
C(2) — H(15)	3.42	0.10	C(4) — H(22)	6.04	0.32	C(7) — C(13)	4.21	0.29	C(12) — H(17)	7.47	0.32
C(2) — H(16)	3.90	0.10	C(4) — H(23)	4.27	0.32	C(7) — H(19)	5.04	0.32	C(12) — H(18)	5.98	0.32
C(2) — H(19)	3.84	0.32	C(5) — C(9)	6.15	0.32	C(7) — H(20)	7.03	0.32	C(13) — H(14)	3.03	0.32
C(2) — H(20)	5.71	0.32	C(5) — C(10)	7.18	0.32	C(7) — H(21)	7.48	0.32	C(13) — H(15)	5.09	0.32
C(2) — H(21)	6.21	0.32	C(5) — C(11)	7.32	0.22	C(7) — H(22)	6.20	0.32	C(13) — H(16)	6.34	0.32
C(2) — H(22)	5.17	0.32	C(5) — C(12)	6.49	0.32	C(7) — H(23)	3.78	0.32	C(13) — H(17)	6.14	0.32
C(2) — H(23)	2.98	0.32	C(5) — C(13)	5.33	0.30	C(8) — H(14)	2.63	0.32	C(13) — H(18)	4.58	0.32
C(3) — C(8)	2.95	0.25	C(5) — H(19)	6.37	0.32	C(8) — H(15)	4.98	0.32	H(14) — H(15)	2.51	0.32
C(3) — C(9)	3.82	0.29	C(5) — H(20)	8.06	0.32	C(8) — H(17)	5.88	0.32	H(14) — H(16)	4.34	0.32
C(3) — C(10)	4.79	0.29	C(5) — H(21)	8.29	0.32	C(8) — H(18)	4.08	0.32	H(14) — H(17)	5.01	0.32
C(3) — C(11)	5.04	0.25	C(5) — H(22)	6.93	0.32						
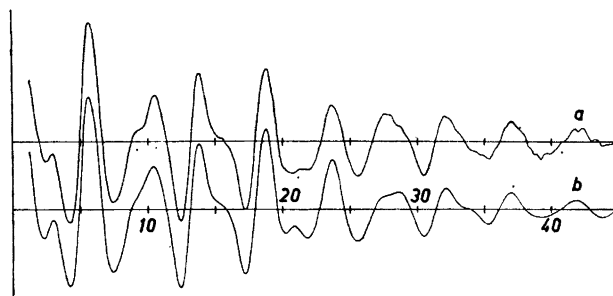
Fig. 10. Experimental (a) and theoretical (b) intensity curves. Theoretical curve molecular
parameters: a: 1.48 Å, b: 1.395 Å, c: 1.11 Å, $\varphi = 45°$ and $\gamma = 118°$.

Experimental and computational errors can cause a deviation in the scale
of one or the other of the radial distribution curves; but this would make all
distances determined from one distribution curve deviate in the same direc-
tion. A comparison of the ring parameters in triphenylmethyl and triphenyl-
methane shows that the C—C bond is shorter and the C—H bond is longer
in the radical than in the methane derivative. The difference curves between
triphenylmethyl and benzene and between triphenylmethane and triphenyl-
methyl (Fig. 5) do indicate changes in the bond length parameters besides
the expected decrease of the $C(1)—C(2)$ bond in the radical. In the regions
around 1.4 Å and 2.5 Å the shape of the difference curves indicates an increase
in the C—H distance and an insignificant decrease in the $C(2)—C(3)$ distance
in the radical as compared to triphenylmethane. In Fig. 7 the difference curve
between the experimental radial distribution curves of triphenylmethane and
triphenylmethyl (curve a) and the same difference curve between the theoreti-
cal distribution curves (curve b) show that the determined molecular param-
eters of the two compounds do give the same difference of the maxima below
approximately 3 Å as is found in the experimental difference curve. Only
average distances in the phenyl groups can be determined in this case and slight
variations in the ring distances could not be detected.

From the u values in Table 1 it can be seen that the contribution of the
ring to ring distances are more heavily damped in this case than in triphenyl-
methane. It has not been possible to determine individual u values for these
distances since the maxima on the outer part of the radial distribution curve
all contain a great number of distances. Greater thermal movements are ex-
pected in the radical than in triphenylmethane where the ortho hydrogens
of the phenyl groups are locked in between the hydrogen on the central carbon
atom and the ortho hydrogen and ortho carbon in the adjacent ring. The un-
certainty in the φ and γ parameters is due to greater movement within the
molecule and can account for the determined value of γ which is slightly differ-
ent from the 120° value expected for a sp^2 hybridized central carbon atom.
The shrinkage effect [7,8] of the out-of-plane-vibrations on the ring to ring
distances can explain the difference of γ from an equilibrium value of 120°.
On the other hand a real deviation of γ from 120° can be explained as well.

Table 2. Shortest ring to ring interatomic distances in triphenylmethyl.

Distance	$\varphi = 40°$			$\varphi = 45°$	
	$\gamma = 116°$	$\gamma = 118°$	$\gamma = 120°$	$\gamma = 116°$	$\gamma = 118°$
H(14)—H(23)	2.95 Å	2.99 Å	3.02 Å	3.25 Å	3.29 Å
C(3) —H(23)	3.08 »	3.06 »	2.97 »	3.30 »	3.29 »
C(3) — C(13)	3.16 »	3.20 »	3.24 »	3.30 »	3.34 »
C(2) — C(13)	3.10 »	3.09 »	3.04 »	3.13 »	3.13 »
C(3) — C(8)	2.87 »	2.93 »	3.04 »	2.88 »	2.95 »

In calculating the resonance energy in a sterically hindered triphenylmethyl radical Adrian [9] found the twist angle φ to have an equilibrium value of approximately 32°. The flat minimum on the curve of the calculated resonance energy *vs.* φ makes the resonance energy change only 1 cal/mole for a 5° deviation in φ. As pointed out by Adrian, small effects which he has neglected would influence the equilibrium value of φ considerably. A molecular-orbital calculation of bond orders in the same paper [9] gave 1.43 Å for the central carbon-carbon distance as compared with 1.48 Å determined here and 1.45 Å in the three-dimensional X-ray crystallographic investigation of the tri-*p*-nitrophenyl-methyl radical.[1] In Table 2 are listed the shortest ring to ring interatomic distances. As in the case of triphenylmethane [4] the twist angle φ does not seem to be determined by steric interactions between ortho-hydrogen on adjacent rings. These distances will range from 2.95—3.0 Å if the uncertainty of the angular parameters is taken into account. The values for the C(3)—H(23) and C(3)—C(13) distances will be 3.0—3.3 Å and 3.2—3.35 Å, respectively. The values listed in Table 2 show that the twist angle φ is not determined by the hydrogen-hydrogen distances but mainly by the carbon-carbon approach of just over 3 Å. All the distances C(3)—C(13), C(2)—C(13) and C(3)—C(8) will have approximately the same values.

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