Electron Diffraction Study of the Molecular Structure of 1,3-Diphenylpropane-1,2,3-trione (Diphenyl Triketone)

György Schultz*[a], István Hargittai[a], Thomas Doerner[b], and Rolf Gleiter[b]

Structural Chemistry Research Group of the Hungarian Academy of Sciences, Eötvös University[a],
Puskin utca 11–13, Pf. 117, H-1431 Budapest, Hungary

Institut für Organische Chemie der Universität Heidelberg[b],
Im Neuenheimer Feld 270, W-6900 Heidelberg, F.R.G.

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The molecular structure of 1,3-diphenylpropane-1,2,3-trione (diphenyl triketone) has been determined by gas-phase electron diffraction at 130°C nozzle temperature. It has been found that the phenyl rings are nearly coplanar with the adjacent carbonyl groups, and the two $C_{ph}-C(O)-C(O)-C(O)$ dihedral angles are -129.5 ± 0.8 and $-107.1 \pm 0.8°$ (0° corresponds to the *syn* form). Bond distances (r_g, Å) and bond angles (deg) with estimated total errors are C–H 1.105 ± 0.006, O=C 1.213 ± 0.003, $\langle C_{ph}-C_{ph}\rangle$ 1.404 ± 0.003, $C_{ph}-C(O)$ 1.478 ± 0.005, C(O)–C(O) 1.558 ± 0.004, $C_{ph}-C(O)-C(O)$ 120.0 ± 0.3, $C_{ph}-C(O)=O$ 120.8 ± 0.4, C(O)–C(O)–C(O) 117.3 ± 0.4, $C_{ph}-C_{ph}(CO)-C_{ph}$ 119.8 ± 0.6. Although there is a general agreement between the gas-phase and crystal molecular structures there are some notable differences. One of the benzene rings is slightly turned about the $C_{ph}-C(O)$ axis in the opposite direction in the gas molecule as compared to the crystal. This causes a marked shortening of the O···H intramolecular contact (to 2.18 Å) between the central oxygen and an *ortho*-hydrogen.

Recent model calculations on the dihedral angles of polyketones predict potential surfaces with broad minima of similar energy content[1]. To understand the factors which influence the structural parameters a comparison between the conformation in the gas phase and in the solid state has been made. So far, mostly solid-state data on vicinal polyketones have been published. Crystal structure studies on 1,3-diphenylpropane-1,2,3-trione (diphenyl triketone) reveal nearly coplanarity of the phenyl groups with the adjacent functions[2], an approximate C_2 symmetry of the molecule, and lack of intramolecular O···H distances below 2.50 Å. It has been shown that the carbon-carbon bonds between the phenyl and carbonyl groups are shorter than those between two carbonyl groups by about 0.06 Å. The $C_{ph}-C(ph)-C(O)$ angle has been found to be significantly larger than the O=C(ph)–C(O) angle (121 vs. 114°) which is unusual and in contrast e.g. to the predictions of the VSEPR model[3]. This is ascribed to a shortened $C_{ph}-C(O)$ distance together with the CO···*ortho*-hydrogen contact (2.50–2.54 Å)[2]. The molecular structures of benzil[4,5], dimesityl triketone[2b], diphenyl tetraketone[2a], dimesityl tetraketone[2b], diphenyl pentaketone, and *tert*-butyl phenylpentaketone[1] have also been determined by a single-crystal X-ray structure analysis. In the gas phase, however, only the molecular structure of benzil is known[6].

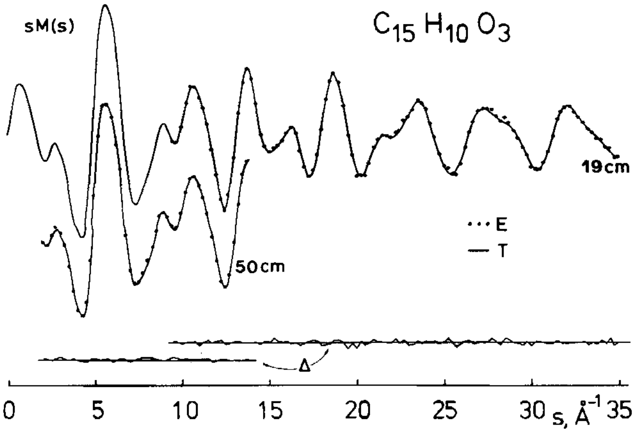

Figure 1. Molecular intensity curves for the two camera distances (E, experimental; T, theoretical). Also shown are the difference curves (E – T)

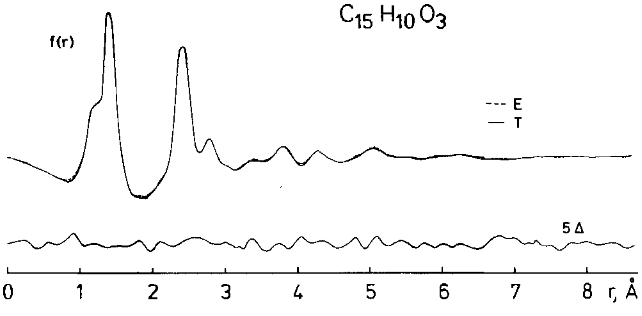

Figure 2. Radial distribution curves (E, experimental; T, theoretical). The difference curve (E – T) is also shown

The main purpose of the present study is to obtain information on the conformational behavior of 1,3-diphenyl triketone in the gas phase.

Experimental

The preparation of 1,3-diphenyl triketone was carried out according to Dayer et al.[7]. The electron diffraction photographs were taken with a modified EG-100A apparatus[8] by using a membrane nozzle system[9]. The nozzle temperature was about 130°C. The accelerating voltage of the electron beam was 60 kV, the electron wavelength $\lambda = 0.049231$ Å was calibrated with a TlCl polycrystal pattern[10]. Nozzle-to-plate distances of about 50 and 19 cm were used, and 7 and 6 plates were selected for analysis from the two distances, respectively. The ranges of the intensity data in the analysis were $2.0 \leqslant s \leqslant 13.75$ Å^{-1} and $9.5 \leqslant s \leqslant 35.0$ Å^{-1}, with data intervals $\Delta s = 0.125$ and 0.25 Å^{-1}, respectively [$s = 4\pi\lambda^{-1}\sin(\Theta/2)$, where Θ is the scattering angle]. For total experimental intensities cf. Tables 3 and 4 at the end of this paper. The experimental and calculated molecular intensities are compared in Figure 1. Experimental and calculated radial distributions are presented in Figure 2.

Structure Analysis

The least-squares method was applied to molecular intensities by using a modified program of Seip et al.[11]. The atomic scattering factors were taken from refs.[12,13]. It was assumed that the bond lengths and bond angles located symmetrically with respect to the central C=O bond were equal; no such assumption was made concerning the angles of torsion. In addition, it was supposed that the bond configurations around carbon atoms were planar and all C=O bonds had the same length. The C−H bonds were assumed to have equal lengths and to bisect the corresponding angles in the benzene ring. The benzene rings together with the carbon atom of the adjacent carbonyl group were supposed to possess C_{2v} symmetry. Under these assumptions the geometry of the molecule was characterized by 16 independent parameters: bond lengths C=O, C5−C6, and C−H; differences between bond lengths: r(C3−C5) − r(C5−C6), r(C3−C5) − r(C2−C3), r(C5−C6) − r(C6−C7), and r(C5−C6) − r(C7−C8); bond angles: C6−C5−C10, C5−C6−C7, C5−C3−C2, C5−C3=O4, and C3−C2−C3′; and angles of torsion C5−C3−C2−C3′, C5′−C3′−C2−C3, C2−C3−C5−C6, and C2−C3′−C5′−C6′. The atoms in the molecule were numbered as shown in Figure 3.

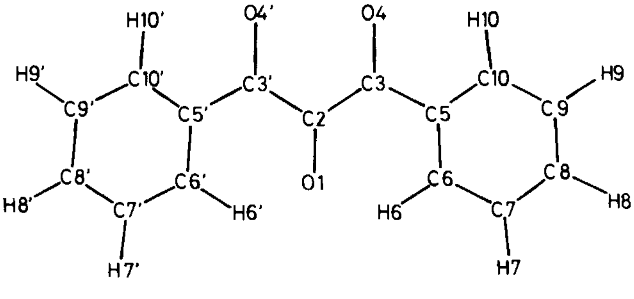

Figure 3. The numbering of atoms in diphenyl triketone

In addition to the geometrical parameters, eight independent mean amplitudes of vibration were refined in groups with other amplitudes. The initial values of amplitudes were partly based on the results obtained for terephthalaldehyde[14]. An empirical relationship[15] between the endocyclic *ipso* (α) and *ortho* (β) angles in the benzene ring, viz. $\Delta\beta = -0.591 \cdot \Delta\alpha - 0.301$, was utilized in the refinements.

The parameters corresponding to the minimum (R factor 4.28%) are presented in Tables 1 and 2 along with the results of the X-ray crystallographic study[2a]. There is general agreement between the conformational properties of the two models except a small but interesting difference in the direction of the torsion of one of the benzene rings. Refinement with an initial value for this angle of the reversed sign resulted in the same model as described above.

We have thoroughly examined the possibility of other models and found only one other local minimum with a higher R factor (5.34%). The conformational properties of this model (the four angles of torsion were −34, −141, −108, and −18° in the order of Table 1) were not only less consistent with the crystal model but also the amounts of benzene torsions were rather large. Furthermore, the C(O)−C(O)−C(O) angle (120.4°) differed from both the "best" gaseous and the crystal structures. We have therefore not further studied this model.

Table 1. Final molecular parameters for diphenyl triketone as obtained from refinement A. Only bonded distances, O···O distances, O···C and C···C distances with multiplicity exceeding unity are presented[a]

Distances and mean amplitudes of vibration (Å)

Parameter	Multiplicity	r_a	l	Key to coupling
C−H	10	1.099(4)	0.082(1)	i
$\langle C_{ph}-C_{ph}\rangle$	12	1.4022(5)	0.0462(8)	ii
O=C	3	1.212(1)	0.045	i
C_{ph}−C(O)	2	1.477(3)	0.0482	ii
C(O)−C(O)	2	1.556(2)	0.0502	ii
C5···C9	4	2.426(3)	0.0579(11)	iii
C6···C10	2	2.426(5)	0.0579	iii
C7···C9	2	2.412(4)	0.0579	iii
C6···C8	4	2.440(1)	0.0579	iii
C5···C8	2	2.820(7)	0.060(2)	iv
C6···C9	4	2.796(4)	0.060	iv
C3···C6	4	2.495(2)	0.0729	iii
C3···C7	4	3.779(3)	0.102(6)	v
C3···C8	2	4.297(6)	0.073(6)	vi
C2···C5	2	2.626(5)	0.0659	iii
C2···C8	2	5.250(5)	0.108(7)	vii
O1···O4	1	3.361(4)	0.122(7)	viii
O1···O4′	1	3.247(5)	0.122	viii
O4···O4′	1	3.661(20)	0.114	v
O1···C3	2	2.419(3)	0.0659	iii
O4···C2	2	2.394(4)	0.0659	iii
O4···C5	2	2.341(5)	0.0539	iii
O4···C8	2	5.026(6)	0.100	vii

Bond angles and angles of torsion (degrees)

C2−C3−C5		120.0(2)
O4−C3−C5		120.8(3)
C2−C3=O4		119.2(3)
C3−C2−C3′		117.3(3)
C6−C5−C10		119.8(4)
C2−C3−C5−C6	(τ1)	−14.1(12)
C5−C3−C2−C3′	(Φ1)	−129.5(5)
C5′−C3′−C2−C3	(Φ2)	−107.1(6)
C2−C3′−C5′−C6′	(τ2)	6.9(15)

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[a] Least-squares standard deviations are given in parentheses as units in the last digit.

Table 2. Geometrical parameters[a)] of 1,3-diphenyl triketone and benzil in gas and crystal phases

Parameter	1,3-Diphenyl triketone		Benzil	
	Gas[b)]	Crystal[c)]	Gas[d)]	Crystal[d)]
C−H	1.099 ± 0.006	[e)]	1.096(11)	[e)]
$C_{ph}-C_{ph}$	1.402 ± 0.003	1.377[f)]	1.399(2)	1.375(9)
O=C	1.212 ± 0.003	1.216(3), 1.213(4), 1.209(3)[g)]	1.220(4)	1.214(9)
$C_{ph}-C(O)$	1.477 ± 0.005	1.469(4), 1.458(4)[g)]	1.488(8)	1.460(9)
C(O)−C(O)	1.556 ± 0.005	1.523(4), 1.522(5)[g)]	1.546(16)	1.542(9)
$C_{ph}-C(O)-C(O)$	120.0 ± 0.3	120.5(2), 121.9(2)[g)]	118.7(9)	120.0(6)
$C_{ph}-C(O)=O$	120.8 ± 0.4	124.7(3), 124.0(3)[g)]	121.4[f)]	124.0(6)
C(O)−C(O)−C(O)	117.4 ± 0.3	117.3(3)		
$C(O)-C(C_{ph})=O$	119.2 ± 0.4	114.8(3), 114.1(3)[g)]	119.9(14)	116.0(6)
α[h)]	119.8 ± 0.6	119.1(3), 118.9(3)[g)]	120[i)]	118.9(6)
τ1[h)]	−14.1 ± 1.7	15.5[j,k)]	9.9(10)	6.5(18)
Φ1[h)]	−129.5 ± 0.8	−125.1[k)]	116.9(34)	108.4(6)
Φ2[h)]	−107.1 ± 0.8	−110.6[k)]		
τ2[h)]	6.9 ± 2.1	4.2[j,k)]		
Reference	This study	[2)]	[6)]	[5)]

[a)] Distances in Å, angles in degrees. In gas phase r_a distances are given. — [b)] Estimated total errors are given as error limits. — [c)] In parentheses standard deviations. — [d)] In parentheses triple standard deviations. — [e)] Not reported. — [f)] Mean value. — [g)] X-ray study provided independent values for these bond lengths/angles. — [h)] See Table 1. — [i)] Assumed value. — [j)] The dihedral angle between the least-squares planes calculated through phenyl C_6-C skeleton and the adjacent carbonyl CCOC skeleton. — [k)] Standard deviation not reported.

In our final calculations a mean C−C distance was refined for the benzene rings as it proved impossible to determine bond length differences not exceeding experimental error.

Discussion

A comparison of the X-ray data of benzil[4)], 1,3-diphenylpropane-1,2,3-triketone[2a)], 1,4-diphenylbutane-1,2,3,4-tetraketone[2)], and 1,5-diphenylpentane-1,2,3,4,5-pentaketone[1)] reveals the following trends: 1) The bond distances between the carbonyl carbon atoms vary between 1.520 and 1.565 Å. These bonds are slightly longer than the single bonds between formal sp^2-sp^2 carbon atoms, such as in butadiene. Such a lengthening might be due to strong dipole-dipole interactions. 2) The carbonyl−oxygen bond lengths vary between 1.188 and 1.225 Å. A slight shortening of the bonds for the inner carbonyl groups in the case of the tetra- and pentaketones is observed. 3) There is no apparent influence of the *ortho*-hydrogen/carbonyl oxygen interaction on the coplanarity of the phenyl and adjacent carbonyl groups. These observations are consistent with the results of the electron diffraction studies of benzil[6)] and 1,3-diphenyl triketone (cf. Table 2).

The conformation of the whole molecule may be characterized by four consecutive angles of torsion along the molecular skeleton: C6−C5−C3−C2, C5−C3−C2−C3′, C3−C2−C3′−C5′, and C2−C3′−C5′−C6′. These angles are −14, −129, −107, 7° and 15, −125, −110, 4° in the gaseous and solid phases, respectively. The first and last angle in the crystal is the dihedral angle between the least-squares planes calculated through the C_6-C skeleton and the adjacent carbonyl CCOC skeleton. Thus, conformational differences only exist in the orientation of the first phenyl ring in the two phases. This difference is accompanied by a short distance between the central oxygen and an *ortho*-hydrogen of the first phenyl group in the gaseous molecule, r(O1···H6) = 2.18 Å, whereas this distance is 2.71 Å in the crystal. All other intramolecular O···H distances exceed 2.50 Å in both phases.

The planes of the two phenyl rings are nearly perpendicular to each other in the gas phase, while the corresponding dihedral angle is about 60° in the solid phase. A stereoview of the gas-phase structure is shown in Figure 4.

Another important gas/solid difference occurs in the bond configuration of the carbonyl carbons adjacent to the phenyl rings. All three angles are 120° within 1° in the gaseous molecule, whereas much larger differences are found in the bond angles in the crystal (see Table 2). One of the O=C−C

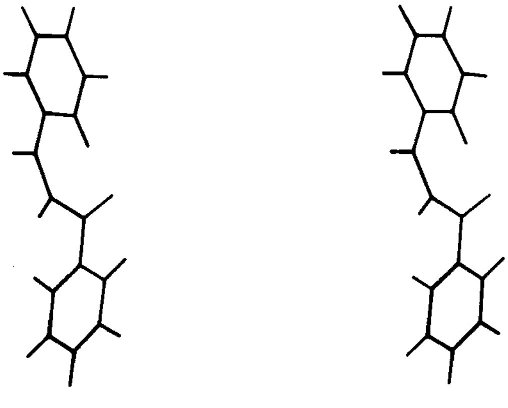

Figure 4. A stereoview of the diphenyl triketone molecule in the gas phase

Table 3. Electron diffraction. Total experimental intensities $I(s)$ for diphenyl triketone, 50 cm camera range, $s_{min} = 2.0$; $s_{max} = 13.75$; $\Delta s = 0.125$ Å^{-1}; the table develops horizontally

.2774	.3152	.3561	.4078	.4669	.5251	.5691	.5921
.6044	.6111	.6104	.6049	.5896	.5739	.5618	.5492
.5477	.5515	.5647	.5903	.6211	.6683	.7199	.7846
.8505	.9124	.9586	.9874	1.0000	.9973	.9843	.9658
.9387	.9086	.8748	.8334	.7906	.7489	.7114	.6796
.6539	.6346	.6245	.6166	.6156	.6134	.6157	.6157
.6196	.6202	.6238	.6275	.6295	.6328	.6331	.6320
.6255	.6211	.6129	.6055	.5981	.5905	.5883	.5876
.5898	.5917	.5952	.5969	.5955	.5927	.5881	.5813
.5745	.5676	.5601	.5527	.5444	.5364	.5263	.5178
.5074	.4998	.4924	.4875	.4853	.4862	.4875	.4919
.4985	.5042	.5110	.5157	.5195	.5200	.5177	

Table 4. Electron diffraction. Total experimental intensities $I(s)$ for diphenyl triketone, 19 cm camera range, $s_{\min} = 9.5$: $s_{\max} = 35.0$; $\Delta s = 0.25\ \text{Å}^{-1}$; the table develops horizontally

						1.0091	.9904
.9909	1.0005	.9999	.9823	.9535	.9262	.8974	.8610
.8265	.7954	.7765	.7793	.7958	.8165	.8276	.8262
.8095	.7847	.7578	.7435	.7330	.7278	.7213	.7161
.7140	.7091	.7002	.6848	.6714	.6621	.6589	.6607
.6663	.6738	.6762	.6736	.6644	.6507	.6341	.6233
.6119	.6085	.6049	.6056	.6071	.6060	.6034	.5993
.5948	.5928	.5896	.5895	.5865	.5848	.5839	.5796
.5743	.5671	.5605	.5525	.5468	.5436	.5389	.5360
.5364	.5377	.5385	.5384	.5377	.5358	.5330	.5308
.5268	.5229	.5214	.5184	.5142	.5105	.5064	.5031
.4985	.4961	.4939	.4928	.4929	.4942	.4952	.4947
.4929	.4916	.4890	.4861	.4837	.4807	.4787	.4761
.4745	.4715	.4701	.4668	.4656			

angles appears to be the smallest, rather than the C–C–C angle, in both phases, in contrast to the predictions of the VSEPR model. However, the deviation is much smaller in the gas phase than in the crystal. The carbonyl bond configurations of gaseous 1,3-diphenyl triketone and benzil are similar to each other (see Table 2). The solid-state structures are also similar.

The *ipso* angles of the benzene rings are consistent in the gaseous molecule and in the crystal and are slightly smaller than 120°.

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CAS Registry Number

1,3-Diphenylpropane-1,2,3-trione: 643-75-4

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