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Does 2-Methylacetophenone Comply with Steric Inhibition of Resonance? A Direct Experimental Proof of Its Nonplanar Conformation from a Joint Ab Initio/Electron Diffraction Analysis

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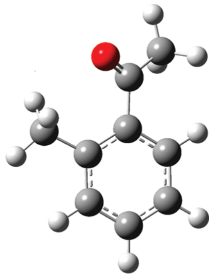

The structure and conformations of 2-methylacetophenone (**1**) have been investigated by ab initio calculations carried out at the MP2(full)/6-311++G** level and by gas electron diffraction (GED). According to both methods, **1** exists predominantly as a form with the $C{=}O$ bond *synclinal* with respect to the C_{ar}−C(O) bond (**1B**), with a torsional angle [C(6)−C(1)−C=O] of 32.7(24)° as determined by GED and 26.0° from MP2(full)/6-311++G**. Calculations also predict the presence of a second conformer, the *anticlinal* structure (**1C**), with $\phi = 140.0°$, with an abundance of less than 6%, an amount hardly detectable by GED. Different DFT computational protocols both support a nonplanar form of the predominant conformer (B2PLYP) and are in contradiction (B3LYP, M052x, B98, B97-D) with this experimental finding. The GED results, supported by the calculations that involve long-range correlation, are in a good agreement with ^{13}C NMR spectroscopic investigations, UV spectra, and dipole moment studies. However, previous claims that assumed steric inhibition of resonance caused by a significantly nonplanar conformation with ϕ close to 90° have been disproved. Steric crowding is evident from the geometrical parameters, particularly from the C(1)−C(2) bond length and from the C(1)−C(2)−C(H_3) and C(2)−C(1)−C(O) bond angles. It is concluded that any explanation of reactivity by steric inhibition of resonance and by other steric factors must be supported by experimental and/or theoretical investigation of the actual molecular shape.

Introduction

The conformations adopted by certain aromatic carbonyl compounds, for example, substituted carboxylic acids and their esters, benzaldehydes and acetophenones, have become increasingly important as a means of explaining their properties using steric inhibition to resonance (SIR) theory.[1] In terms of this theory, the observable quantities are directly correlated with the torsion angle, ϕ, between the aromatic ring and the carbonyl

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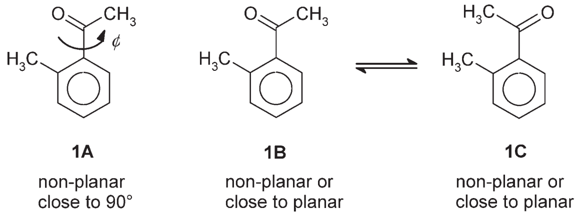
plane,[1,2] as shown, for instance, for 2-methylacetophenone in the nonplanar conformation **1A**. The angle, ϕ, itself can be derived either from observable properties (mostly from electronic,[3] infrared,[4] ^{13}C NMR,[5] and ^{17}O NMR[6] spectra or, exceptionally, from other quantities[7]) or from semiempirical[2c,6,8] and ab initio[9,10] calculations. According to the classic theory,[3] it was assumed[1,5−7] that ϕ varies continuously between 0 and 90° according to the strength of the steric hindrance. However, this view was recently challenged by us[2,10,11] on the basis that certain less-hindered compounds evidently exist in planar conformations and as an equilibrium of two conformers, as shown in **1B** $\rightleftharpoons$ **1C**. Besides the X-ray analysis of 2-methyl-5-nitrobenzoic acid,[10] the most important direct experimental proof was the gas electron diffraction (GED) structure of methyl 2-methylbenzoate.[11] However, this study of a compound with 21 atoms, two axes of rotation, and two rotamers in equilibrium was already at the limits of possibility of the GED method.



In this study, we have analyzed GED data for 2-methylacetophenone to determine whether the most stable conformation is the nonplanar form **1A** (ϕ close to 90°) or two planar (ϕ quite close to 0 or 180°) forms **1B** and **1C** in equilibrium. Since the principle of SIR was first proposed, derivatives of acetophenone have been of great importance, and the variable angle, ϕ, has been central to these efforts.[3] The most studied example is 2-methylacetophenone, assumed to have a single nonplanar structure, not only in the fundamental paper[3] but also in later work;[4,5a,6a,7,12] the angle ϕ was given values between 30 and 41°, and SIR was often accepted as the explanation for nonplanarity.[4,5a,6a,7] Only in one previous study was the equilibrium **1B** $\rightleftharpoons$ **1C** taken into consideration,[13] and on two occasions the forms **1B**[14] or **1C**[15] were considered as the sole component.

Results and Discussion

The Conformational Problem. The conformations of 2-methylacetophenone (**1**) (for numbering, see Figure 1) were determined by means of a combined approach based on high-level ab initio calculations and gas electron diffraction, referred to as the SARACEN method.[16]

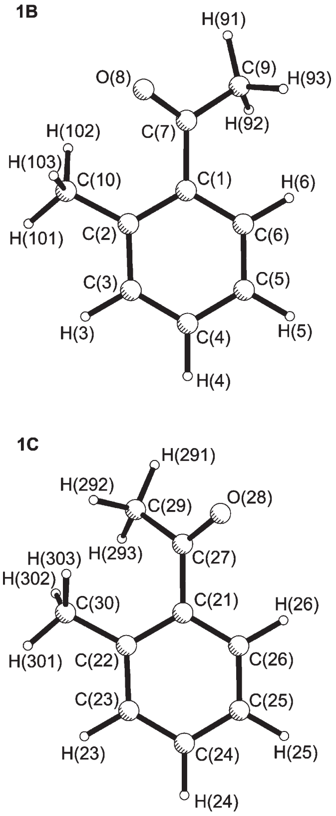


FIGURE 1. Molecular structure, including atom numbering, for **1B** and **1C**.

Ab initio calculations at the MP2(full)/6-311++G** level yielded not only the minimum energy conformation (**1B**) but also the second conformation (**1C**) and the energy difference between the two. The results at this level show an unambiguous preference for an equilibrium of two slightly nonplanar conformations, that is, one *synclinal* conformer (*sc*, **1B**, $\phi_{9\text{-}7\text{-}1\text{-}6} = 26°$) and one *anticlinal* conformer (*ac*, **1C**, $\phi_{29\text{-}27\text{-}21\text{-}26} = 140°$), with the first minimum appearing to be quite deep (see Figure 2).

Figure 2 indicates three barriers, $\phi = 0, 180$, and 95°, with the latter being a transition state on going from **1B** to **1C**. From the energy difference of 7.0 kJ mol^{-1}, the population of the *sc* rotamer **1B** can be estimated to be 94%. Previous calculations [B3LYP/6-311+G(d,p)], which were undertaken in connection with an investigation of the UV spectra of substituted acetophenones, agree in this respect, indicating that 99% of such a form should be present.[17] In terms of ϕ,

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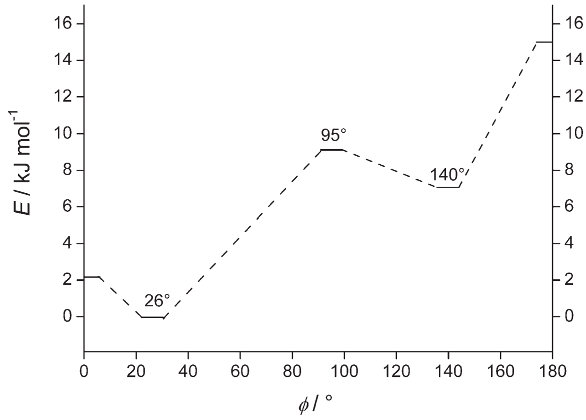

FIGURE 2. Calculated [MP2(full)6-311++G**] relative energies of conformers for **1** in kJ mol^{-1}.

an estimated value of 41° results from UV spectra in contrast to the B3LYP/6-311+G(d,p) value of 0.5[17] or 0° as obtained with the newly introduced functional M052x used in this study.[18] Becke's B98 functional behaved in a similar way to M052x; that is, the twist was 0°. Additionally, Grimme's B97-D dispersion corrected functional using the 6-311++G(d,p) basis set revealed this angle to be 1.2°; that is, dispersion contribution is very unlikely to be responsible for the twist. However, employing Grimme's double-hybrid B2PLYP functional with a fine grid (75 radial shells with 302 angular points per shell), which contains some MP2-like correlation, the twist converged to ca. 16°. Note that employing the ultrafine grid changed the twist negligibly (15.5°). It seems that a long-range correlation effect included within the perturbation theory might be the driving force for a nonplanar form. MP2 calculations using the frozen-core approximation (fc) and the cc-pVTZ basis also prefer a nonplanar conformation of the predominant form ($\phi = 10°$), although to a lesser extent. As a consequence, the barrier with respect to a form with $\phi = 0°$ is extremely shallow, just 0.03 kJ mol^{-1}. The inclusion of diffuse functions seems to be essential for reproducing the experimental value and more important than using the full core in the MP2 model chemistry [MP2(fc)/6-311++G** provided the twist to be 27.5° with the barrier with respect to $\phi = 0°$ of 2.1 kJ mol^{-1}].

Due to the low overall symmetry of **1** (**1B** and **1C** are both C_1 symmetric), a large number of geometric parameters are required to describe both forms. Because there is not enough information in the experimental data, differences between many similar distances in the GED model were restrained using the SARACEN method[16] taking values from the above calculations. The uncertainty of a restraint is estimated from the degree of convergence throughout a series of calculations. In order to determine some of the structural parameters experimentally, the restraints are necessary. The torsional angles for the conformations determined by GED represent the absolute average values of the deviation and may differ from the computed values.

Molecular Model and Refinement of the Structure. Taking previous structural studies of **1** into account, we used a two-conformer model to analyze the GED data and introduced some simplifications into the geometry of the benzene ring. Guided by the MP2(full)/6-311++G** calculations (used in a similar study of methyl 2-methylbenzoate[11] and found to be closest in terms of ϕ to other experimental proofs), we reduced the number of C−C distances within the ring as if it had a mirror plane bisecting r[C(1)−C(2)] and r[C(4)−C(5)]. The computed distances at MP2(full)/6-311++G** that are considered to be equal in the model differed by less than 0.3 pm. At the same level, the computed bond angles that are assumed to be identical in the model differed by less than 0.3°. Although we reduced the number of C−C distances required to describe the C_6 ring (see above), we still used four different CCC angles. A tilt angle of the CH_3 group within the CH_3CO substituent in each form (i.e., the deviation of the local C_3 axis from its associated C−C bond) was considered in the model. However, C_3 symmetry was assumed for both conformers for the methyl groups attached to the ring, with calculations providing strong support for this assumption. Table 1 provides further details of the molecular model. Note that due to the low percentage of the second form (6% predicted by MP2 calculations) many parameters relating to the second conformer were fixed to be identical to those of the first conformer. The exceptions to this assumption were the tilt angle (p_{21}), the CCCO dihedral angle (p_{23}), and two methyl torsions (p_{25} and p_{27}) for conformer **2**.

In total, 27 independent parameters were defined to describe the two forms of **1**. One additional parameter (p_{28}) was included to vary the relative amounts of forms **1B** and **1C**. The refinement of the majority of parameters proceeded smoothly, with parameters that could otherwise not be refined restrained flexibly during the refinement process. Inclusion of vibrational amplitudes (u) associated with nonbonded distances to hydrogen atoms led to a false minimum where p_{22} was ca. 56°, caused by some unrealistic values of vibrational parameters. Such amplitudes were therefore fixed at the computed values during the refinements. The angles C(1)C(7)O(8) and C(1)-C(7)C(9) (p_{10} and p_{11}) when refined went against all calculations as p_{10} became smaller than p_{11}; a restraint was consequently placed on the difference between these two parameters. We then explored the dependence of the R factor on the amount of the first conformer. However, the change in R factor on varying p_{28} about its calculated value was negligible (note that the free energy difference gives p_{28} as 93%), highlighting the limited information in the data about the presence of the second form. The parameter p_{28} was therefore fixed at its MP2(full)/6-311++G** value, as was the case in the study of methyl 2-methylbenzoate.[11] Many refinements were also tried with different starting values (e.g., those provided by various functionals) for p_{22}. Such trials always arrived at ca. 32°, with no appreciable changes in the rest of parameters; that is, the geometry characterized by this torsional angle appears to be a true minimum.

The success of the final refinement can be assessed on the basis of the difference between the experimental and calculated [curve a] radial distribution curves (Figure 3); the other two difference curves demonstrate that is not possible to determine from the GED data how much of the second form (or any other minor form) is present, regardless of how the amount of such a form is predicted. Figure S1 in the Supporting Information offers a similar comparison between the experimental and calculated molecular scattering curves. Table S1 in the Supporting Information provides

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TABLE 1. Geometrical Parameters from the r_{h1} Refinement of a Mixture of two C_1 Conformers of 1[a]

		GED[b] (r_{h1})	MP2[c] (r_e)	restraint
	Independent			
p_1	r[C(7)−O(8)]	125.3(6)	122.3	−−
p_2	{r[C(1)−C(7)] + [C(7)−C(9)] + [C(2)−C(10)]}/3	149.5(4)	150.8	−−
p_3	r[C(7)−C(9)] − r[C(1)−C(7)]	2.1(5)	2.1	2.1(5)
p_4	r[C(7)−C(9)] − r[C(2)−C(10)]	1.0(5)	1.1	1.1(5)
p_5	{r[C(1)−C(2)] + 2 × [C(1)−C(6)] + 2 × [C(5)−C(6)]}/5	140.2(2)	140.3	−−
p_6	r[C(1)−C(2)] − r[C(1)−C(6)]	0.7(5)	0.7	0.7(5)
p_7	r[C(1)−C(2)] − r[C(5)−C(6)]	1.7(4)	1.6	1.6(5)
p_8	{6 × $r[\mathrm{C_{Me}}^{d}-\mathrm{H}]$ + 4 × $r[\mathrm{C_{Vi}}^{e}-(\mathrm{H})]$}/10	111.5(4)	109.0	109.0(10)
p_9	$r[\mathrm{C-H}]_{\mathrm{Me}}{}^{d} - r[\mathrm{C-H}]_{\mathrm{Vi}}{}^{e}$	0.6(5)	0.7	0.7(5)
p_{10}	∠[C(1)C(7)O(8)]	122.0(8)	121.3	−−
p_{11}	∠[C(1)C(7)C(9)]	119.7(8)	117.9	−−
p_{12}	{∠[C(1)C(2)C(10)] + ∠[C(2)C(1)C(7)]}/2	121.2(4)	122.2	122.2(10)
p_{13}	∠[C(1)C(2)C(10)] − ∠[C(2)C(1)C(7)]	1.8(10)	2.1	2.1(10)
p_{14}	{3 × ∠[C(2)C(1)C(6)] + ∠[C(1)C(6)C(5)] + ∠[C(1)C(2)C(3)] + ∠[C(2)C(3)C(4)]}/6	120.0(2)	120.1	−−
p_{15}	∠[C(2)C(1)C(6)] − {∠[C(1)C(6)C(5)] + ∠[C(1)C(2)C(3)] + ∠[C(2)C(3)C(4)]}/3	−1.0(5)	−0.5	−0.5(5)
p_{16}	∠[C(1)C(6)C(5)] − {∠[C(1)C(2)C(3)] + ∠[C(2)C(3)C(4)]}/2	−3.9(5)	−3.7	−3.7(5)
p_{17}	∠[C(1)C(2)C(3)] − ∠[C(2)C(3)C(4)]	−1.2(5)	−1.0	−1.0(5)
p_{18}	∠[C(4)C(5)H]	120.0	120.0	−−
p_{19}	∠$[\mathrm{CC_{Me}}^{d}\mathrm{H}]$	110.0	110.0	−−
p_{20}	∠$[\mathrm{CH_3-C({=}O)\ tilt}]_1{}^{f}$	2.1	2.1	−−
p_{21}	∠$[\mathrm{CH_3-C({=}O)\ tilt}]_2{}^{g}$	1.3	1.3	−−
p_{22}	ϕ[C(2)C(1)C(7)O(8)][h]	32.7(21)	26.0	−−
p_{23}	ϕ[C(22)C(21)C(27)O(28)][i]	140.4(105)	140.0	140.0(100)
p_{24}	ϕ[C(1)C(7)C(9)H(92)]	47.2(48)	47.4	47.4(5)
p_{25}	ϕ[C(1)C(2)C(10)H(101)]	38.9(50)	45.3	45.3(5)
p_{26}	ϕ[C(21)C(27)C(29)H(293)]	−28.4(53)	−28.4	−28.4(5)
p_{27}	ϕ[C(21)C(22)C(30)H(303)]	−44.6(53)	−44.6	−44.6(5)
p_{28}	% of **1B**	94	94	−−
	Dependent			
p_{29}	rC(1)−C(2)	141.3(4)	141.5	−−
p_{30}	rC(1)−C(6)	140.5(3)	140.6	−−
p_{31}	rC(5)−C(6)	139.5(3)	139.5	−−
p_{32}	rC(1)−C(7)	148.4(6)	149.8	−−
p_{33}	rC(2)−C(10)	149.5(6)	150.8	−−
p_{34}	rC(7)−C(9)	150.5(5)	151.6	−−
p_{35}	rC(4)−C(5)	139.2(5)	139.7	−−
p_{36}	∠[C(1)C(2)C(3)]	117.8(4)	117.9	−−
p_{37}	∠[C(1)C(6)C(5)]	121.2(4)	121.1	−−
p_{38}	∠[C(2)C(1)C(6)]	119.5(3)	119.9	−−
p_{39}	∠[C(2)C(3)C(4)]	122.5(4)	122.1	−−
p_{40}	∠[C(1)C(2)C(10)]	122.1(7)	123.2	−−
p_{41}	∠[C(2)C(1)C(7)]	120.3(5)	121.1	−−
p_{42}	$p_{10} - p_{11}$	−2.3(9)	−3.4	−3.4(10)

[a] Distances (r) are in picometers, and angles (∠) and dihedral angles (ϕ) are in degrees. [b] Figures in parentheses are the estimated standard deviations of the last digits; the GED parameters are of the r_{h1} type, which are corrected for the effects of vibration. [c] MP2(full)/6-311++G**; r_e are equilibrium distances. [d] Bond lengths within the two methyl groups. [e] Bond lengths with the benzene ring. [f] Positive values resulted in a smaller C(7)C(9)H(91) angle than the other two within the CH_3CO group. [g] Positive values resulted in a smaller C(27)C(29)H(291) angle than the other two within the CH_3CO group. [h] Positive values denote a clockwise rotation from the eclipsed C(2)C(1)C(7)O(8) position. [i] Positive values denote a clockwise rotation from the eclipsed C(22)C(21)C(27)O(28) position.

a complete list of interatomic distances, amplitudes of vibration, and distance corrections from the final refinement. A portion of the least-squares correlation matrix is given in Table S2.

The torsional angles (p_{13}, p_{14}) obtained by the MP2(full) calculations, which predict nonplanar forms (26.0 and 140.0°, respectively), and those determined experimentally [32.7(21)°, and the restrained value 140.4(105)°, respectively] differ only slightly. However, a direct comparison must be taken with caution due to different physical interpretations. In essence, GED gives a weighted average structure over all populated vibrational states, whereas the computational methods provide the equilibrium structure (see Table 1). It is common in GED studies to correct the distances for the effects of these vibrations to get them in the form comparable with the optimized distances. The r_{h1} approximation is based on two corrections, perpendicular (k) and parallel to the vector r between two atoms (u^2/r, where u is the amplitude of vibration of this pair). The link between the "raw" GED distances (r_a) and the corrected ones is therefore $r_a = r_{h1} - u^2/r + k$.

Structural Details. Since there is overall agreement between the structures derived from ab initio and from GED, the discussion will apply equally to both sets of results. The possibility of significant ring distortions and widening of the adjoining angles has been generally underestimated or omitted in previous discussions of SIR. However, a joint GED/ab initio investigation of 1-CH_3COO-2-CH_3-C_6H_4 did pay attention to the possibility of these geometrical features and found a lengthening of the C(1)−C(2) distance in the ring and a widening of the adjacent C(2)−C(1)−C(7) and C(1)−C(2)−C(10) angles, as well as other deformations of the ring.[11] In **1**, the same geometrical features are observed (see Table 1). There is some evidence of an attractive contact O(8)···H(103) in **1B** of the

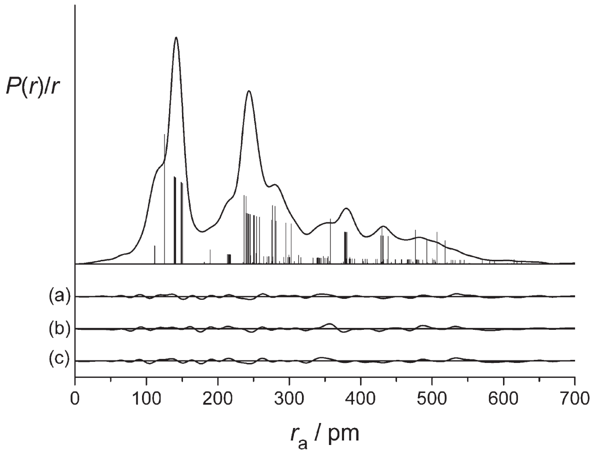

FIGURE 3. Experimental and three difference (experimental minus theoretical) radial distribution curves, $P(r)/r$, attributed to (a) a mixture of two C_1 forms, (b) 0% of the major conformer, and (c) 100% of the major form of **1**. Before Fourier inversion, the data were multiplied by $s \times \exp(-0.00002s^2)/(Z_C - f_C)(Z_O - f_O)$.

GED structure (i.e., 268.4(93) pm), which is only slightly larger than the sum of the corresponding van der Waals radii ($129_O + 116_H = 245$ pm). This separation is computed to be 261.6 pm at MP2(full)/6-311++G**.

Conclusions

An analysis of the electron diffraction data for the vapor of **1** revealed that GED and MP2 calculations agreed that 2-methylacetophenone is very likely to exist predominantly in one nonplanar conformer. Other experimental tools strongly support this observation. Whereas some DFT functionals (B3LYP, B98, B97-D, M052x) give opposing results, particularly with respect to the conformation of the predominant form, there is a double hybrid functional (B2PLYP) that more or less supports GED and MP2 values of the twist; that is, it predicts **1** in the form that is qualitatively anticipated by the theory of steric inhibition of resonance for all ortho derivatives. The structural study of **1** extends this principle quantitatively, although SIR is usually associated with values of ϕ close to 90°. In any further application of this theory, it is advisible to determine the actual conformation of each molecule by *direct* methods as was done in the present work.

Experimental Section

Synthesis. 2-Methylacetophenone was prepared from 2-methylbenzonitrile and methylmagnesium iodide[19] in connection with an NMR study,[20] and its purity was checked using ^{1}H and ^{13}C NMR.[20]

Gas Electron Diffraction. The electron diffraction data were recorded with the Balzers Eldigraph KD-G2 instrument at the University of Oslo[21] on Kodak Electron Image plates with a nozzle-tip temperature of about 295 K. The accelerating voltage of the electron beam was 42 kV, and the voltage/distance calibration was performed using benzene as a reference. The weighting points for the off-diagonal weight matrices, correlation parameters, and scale factors for both camera distances are given in Table S3 in the Supporting Information. The least-squares refinement process was carried out using the ed@ed v3.0 program[22] employing the scattering factors of Ross et al.[23]

Computational Details. Geometry optimizations began at the HF level for all forms and the transition state with respective symmetry constraints (C_s for $\phi = 0$ and 180°, C_1 for both minima and TS) using standard ab initio methods.[24] Second derivative analysis confirmed the two conformations to be minima on the respective potential energy hypersurfaces. The geometry optimizations were run using various model chemistries (ab initio, B3LYP, M052x), and the level that includes the electron correlation based on Møller–Plesset perturbation theory (MP2) and denoted as MP2(full)/6-311++G** was considered to be the best. These calculations were carried out using the Gaussian 03 program.[25] Gaussian 09 was employed for generating B98, B97-D, and B2PLYP geometries.[26] Force constants calculated at the MP2(full)/6-311++G** level were used with the SHRINK program[27] to give starting values for the amplitudes of vibration and first-order curvilinear distance corrections for each atom pair. With these distance corrections, the refined structural parameters are described as r_{h1}. Cartesian coordinates for both the final GED structure and those calculated at the MP2(full)/6-311++G** level are given in Tables S4 and S5 in the Supporting Information, respectively.

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Supporting Information Available: Details of the GED experiments; interatomic distances, refined and calculated amplitudes of vibration and curvilinear corrections for the GED structure of **1**; least-squares correlation matrix for the refined GED structure of **1**; GED and calculated coordinates (and energy) for **1**; molecular scattering intensity and difference curves for the GED refinement of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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