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# Intramolecular Hydrogen Bonding and Molecular Structure of 2,5-Dihydroxyterephthalaldehyde and 4,6-Dihydroxyisophthalaldehyde: A Gas-Phase Electron Diffraction and *ab Initio* Molecular Orbital Study

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The molecular structure of 2,5-dihydroxyterephthalaldehyde has been determined from a joint electron diffraction/*ab initio* investigation, and the molecular structure of 4,6-dihydroxyisophthalaldehyde has been obtained from *ab initio* calculations at the MP2/6-31G\* level. There is considerable intramolecular hydrogen bonding in these structures manifested by the O···H and O···O distances as well as by the structural changes in the rest of the molecule. These changes are consistent with the notion of resonance-assisted hydrogen bonding. The hydrogen bonding is somewhat stronger in 4,6-dihydroxyisophthalaldehyde than in 2,5-dihydroxyterephthalaldehyde, and this difference may be linked to the difference in the mutual positioning of the interacting formyl and hydroxy groups in these molecules.

## Introduction

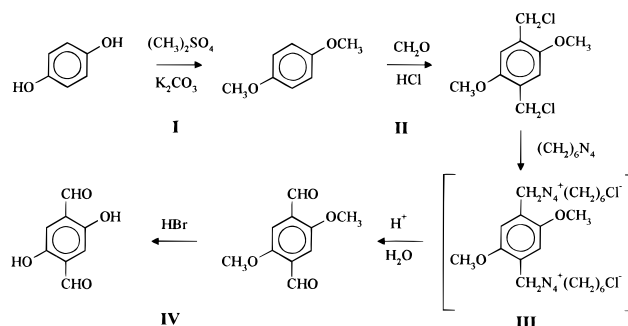
Our recent investigations of the molecular structures of a series of *ortho*-substituted benzene derivatives including 2-nitroresorcinol,<sup>2,3</sup> 2-nitrophenol,<sup>4</sup> 4,6-dinitroresorcinol,<sup>5</sup> and salicylaldehyde<sup>6</sup> by electron diffraction and *ab initio* calculations indicated considerable intramolecular hydrogen bonding in these molecules assisted by substantial structural changes in the rest of the molecule as compared with the respective parent molecules of phenol<sup>3,7</sup> and nitrobenzene<sup>3,8</sup> and phenol<sup>3,7</sup> and benzaldehyde.<sup>6</sup> The barrier to internal rotation of the nitro group in the *o*-nitrophenols is about 10 kJ/mol higher than in nitrobenzene as a consequence of the restraining effect of the intramolecular hydrogen bond formation.<sup>9</sup> The barrier to internal rotation in salicylaldehyde was found to be also about 10 kJ/mol higher than in benzaldehyde.<sup>6</sup> Our recent *ab initio* calculations on 4,6-dinitroresorcinol and 2,5-dinitrohydroquinone,<sup>10</sup> i.e., the nitro analogs of the present title molecules, revealed some indications of increased intramolecular interactions in 4,6-dinitroresorcinol as compared with 2,5-dinitrohydroquinone. As a continuation of our research into the geometrical consequences of intramolecular hydrogen bond formation, we report here the results of electron diffraction and *ab initio* study of 2,5-dihydroxyterephthalaldehyde and the results of *ab initio* calculations on 4,6-dihydroxyisophthalaldehyde.

## Experimental Section

**Synthesis.** The sample of 2,5-dihydroxyterephthalaldehyde was synthesized according to Scheme 1. Steps I, II, and IV are different from those reported in refs 11, 12, and 13, respectively.

**1,4-Dimethoxybenzene.** A mixture of 40 g (0.36 mol) of 1,4-dihydroxybenzene, 400 mL of acetone, 80 g (0.57 mol) of powdered dry potassium carbonate, and 80 mL (106 g, 0.84 mol) of dimethyl sulfate was boiled under reflux with stirring

SCHEME 1



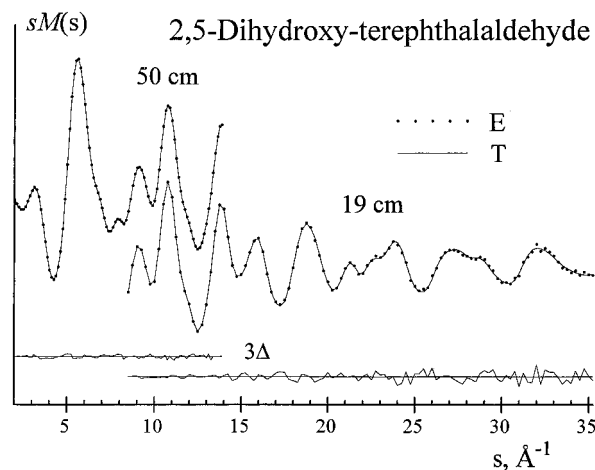
for 20 h. Then 250 mL of water was added to the still hot mixture, which was further stirred for 90 min. The mixture was then diluted with a solution of 12 g of (0.21 mol) potassium hydroxide in 25 mL of water. The product was extracted first by mixture of 100 mL of ethyl acetate and 50 mL of ether and then by 50 mL of pure ether. The combined organic phase was dried by Na<sub>2</sub>SO<sub>4</sub>, the solvent was evaporated, and the rest was fractionated. The fraction boiling in the 170–215 °C interval (40 g, 80.5%) was collected and fractionated again. Yield of the product was 36.8 g (73.3%), bp 212–214 °C, mp 55 °C (lit.<sup>11</sup> bp 216.6 °C, mp 56 °C).

**1,4-Dimethoxy-2,5-bis(chloromethyl)benzene.** The substance was prepared in the way described in ref 14.

**2,5-Dimethoxyterephthalaldehyde.** A mixture of 24.1 g (0.10 mol) of 1,4-dimethoxy-2,5-bis(chloromethyl)benzene and 30 g (0.21 mol) of hexamethylenetetramine in 200 mL of chloroform was boiled for 30 min and then left at room temperature overnight. The solvent was removed under reduced pressure, and the rest was boiled with stirring in 320 mL of 50% aqueous acetic acid for 12 h. Then 25 mL of saturated hydrochloric acid was added to the mixture, and boiling continued further for 8 h in an oil bath at 120 °C. The precipitated product was filtered and washed with water and alcohol. Yield of the product was 2.1 g (10.5%), mp 201 °C (lit.<sup>12</sup> mp 207 °C). From the filtrate an additional 0.8 g of the product could be obtained; its mp was 200 °C. The substance was used for the next step without purification.

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**Figure 1.** Experimental (E) and theoretical (T) molecular intensities and three times their differences ( $3\Delta$ ) for 2,5-dihydroxyterephthalaldehyde. 50 cm and 19 cm refer to the two camera ranges used in the experiments (cf. Table 1).

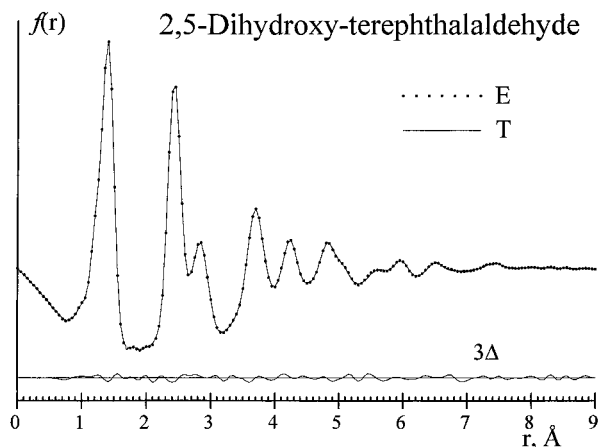
**TABLE 1: Experimental Conditions for 2,5-Dihydroxyterephthalaldehyde**

no. of plates	camera dist., mm	nozzle temp, °C	wavelength, Å	data intervals, Å <sup>-1</sup>	data steps, Å <sup>-1</sup>
7	501.4	152	0.049 53	2.000–13.875	0.125
5	192.4	152	0.049 53	8.50–35.25	0.25

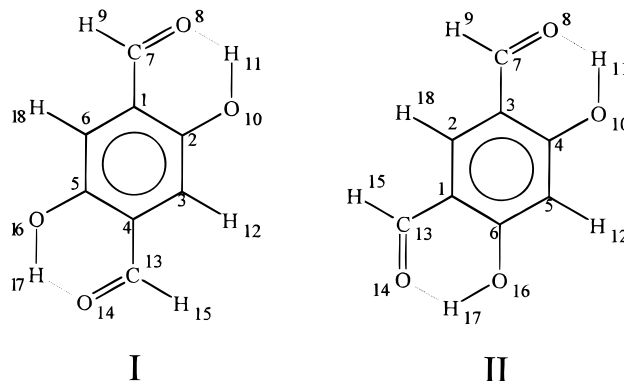
**2,5-Dihydroxyterephthalaldehyde.** To 2.1 g (10.8 mmol) of 2,5-dimethoxyterephthalaldehyde was added 30 mL of 48% aqueous hydrobromic acid, and the mixture was boiled under reflux with stirring in an oil bath at 130 °C for 35 h. The mixture was then evaporated at reduced pressure to approximately one-fourth of the initial volume, and 50 mL of 48% aqueous hydrobromic acid was added. Then the mixture was diluted by adding 50 mL of acetic anhydride in portions with shaking. It was further boiled for another 25 h. The solvent was removed under reduced pressure, and the product was extracted with benzene. After the organic phase was evaporated and benzene was removed the rest (2,5-dihydroxyterephthalaldehyde, 0.8 g, 44.7%) was purified by sublimation in vacuum (0.5 Torr) in an oil bath at 160–180 °C, yielding 0.5 g (25.7%), mp 251–252 °C (lit.<sup>13</sup> mp 258–260 °C). For the purpose of the electron diffraction experiment the substance was sublimed twice, and its purity was checked by thin layer chromatography.

**Electron Diffraction Experiment.** The electron diffraction photographs of 2,5-dihydroxyterephthalaldehyde were recorded in our modified EG-100A apparatus<sup>15</sup> with a membrane nozzle system<sup>16</sup> from two nozzle-to-plate distances. Some of the experimental conditions are summarized in Table 1. The experimental total intensities are given as Supporting Information and may also be obtained from the authors. The atomic electron scattering factors were taken from available compilations.<sup>17</sup> The experimental and theoretical molecular intensities and radial distributions are shown in Figures 1 and 2. The numbering of atoms is presented in Figure 3.

**Ab Initio Calculations.** The ab initio molecular orbital calculations were carried out using the GAUSSIAN 94 series of programs.<sup>18</sup> The polarized standard 6-31G\* basis set<sup>19</sup> was used throughout. Initially, RHF/6-31G\* optimizations, as well as frequency analyses, were performed for both 2,5-dihydroxyterephthalaldehyde (I) and 4,6-dihydroxyisophthalaldehyde (II) to confirm that the computed planar structures are indeed stable states. The calculations for these molecules were then followed by second-order Møller–Plesset<sup>20</sup> optimizations with only valence orbitals active (MP2(FC)/6-31G\*) to include the effect



**Figure 2.** Experimental (E) and theoretical (T) radial distributions and three times their difference ( $3\Delta$ ) for 2,5-dihydroxyterephthalaldehyde.



**Figure 3.** The numbering of atoms for 2,5-dihydroxyterephthalaldehyde (I) and 4,6-dihydroxyisophthalaldehyde (II).

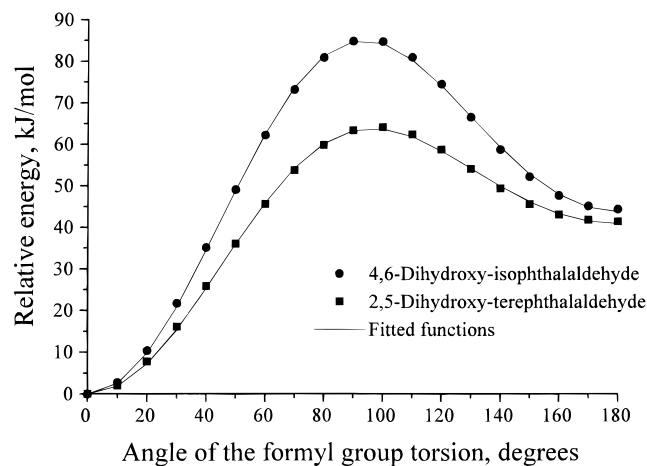
**TABLE 2: 2,5-Dihydroxyterephthalaldehyde: Computed Geometries<sup>a</sup>**

parameter	HF/6-31G*	MP2(FC)/6-31G*
C <sub>1</sub> –C <sub>2</sub>	1.4009	1.4191
C <sub>2</sub> –C <sub>3</sub>	1.3823	1.3931
C <sub>3</sub> –C <sub>4</sub>	1.3897	1.4020
C <sub>3</sub> –H	1.0751	1.0885
C <sub>6</sub> –C <sub>1</sub> –C <sub>2</sub>	120.57	120.66
C <sub>1</sub> –C <sub>2</sub> –C <sub>3</sub>	118.03	118.47
C <sub>2</sub> –C <sub>3</sub> –C <sub>4</sub>	121.40	120.87
C <sub>1</sub> –C <sub>6</sub> –H	120.23	120.50
C <sub>1</sub> –C <sub>7</sub>	1.4775	1.4645
C=O	1.1969	1.2388
C <sub>7</sub> –H	1.0908	1.1057
C <sub>1</sub> –C <sub>7</sub> =O	124.34	124.19
C <sub>1</sub> –C <sub>7</sub> –H	115.55	116.19
C <sub>2</sub> –C <sub>1</sub> –C <sub>7</sub>	121.18	120.67
C–O	1.3380	1.3543
O–H	0.9538	0.9872
C–O–H	110.29	107.11
C <sub>1</sub> –C <sub>2</sub> –O	123.80	123.12
O <sub>8</sub> ···H <sub>11</sub>	1.9130	1.8151
O <sub>8</sub> ···O <sub>10</sub>	2.7146	2.6866
O–H···O <sub>8</sub>	140.10	145.37
C=O···H <sub>11</sub>	100.30	99.54
energy (au)	–605.882 410 1	–607.599 388 2

<sup>a</sup>  $r_e$  equilibrium bond lengths (Å) and angles (deg).

of electron correlation into the calculations. The results of the computations are presented in Tables 2 and 3.

Potential energy curves corresponding to the rotation of the formyl groups were calculated for both molecules at the HF/6-31G\* level. In these single-point total energy calculations the molecular geometries were assumed, while one of the formyl groups was rotated stepwise in the interval 0–180° with 10°



**Figure 4.** Potential energy curve of internal rotation of the formyl groups in 2,5-dihydroxyterephthalaldehyde and 4,6-dihydroxy isophthalaldehyde calculated at the HF/6-31G\* level.

**TABLE 3: 4,6-Dihydroxyisophthalaldehyde: Computed Geometries<sup>a</sup>**

parameter	HF/6-31G*	MP2(FC)/6-31G*
C <sub>6</sub> –C <sub>1</sub>	1.4197	1.4236
C <sub>1</sub> –C <sub>2</sub>	1.3840	1.3940
C <sub>5</sub> –C <sub>6</sub>	1.3841	1.3934
C <sub>5</sub> –H	1.0722	1.0854
C <sub>2</sub> –H	1.0777	1.0916
C <sub>5</sub> –C <sub>6</sub> –C <sub>1</sub>	120.48	120.29
C <sub>6</sub> –C <sub>1</sub> –C <sub>2</sub>	118.15	118.84
C <sub>1</sub> –C <sub>2</sub> –C <sub>3</sub>	122.56	121.59
C <sub>4</sub> –C <sub>5</sub> –C <sub>6</sub>	120.18	120.16
C <sub>3</sub> –C <sub>2</sub> –H	118.72	119.21
C <sub>6</sub> –C <sub>5</sub> –H	119.91	119.92
C <sub>3</sub> –C <sub>7</sub>	1.4585	1.4568
C <sub>7</sub> =O	1.2017	1.2400
C <sub>7</sub> –H	1.0921	1.1062
C <sub>3</sub> –C <sub>7</sub> =O	124.79	124.36
C <sub>3</sub> –C <sub>7</sub> –H	115.51	116.11
C <sub>4</sub> –C <sub>3</sub> –C <sub>7</sub>	121.62	121.20
C–O	1.3186	1.3456
O–H	0.9577	0.9908
C–O–H	110.51	107.22
C <sub>3</sub> –C <sub>4</sub> –O	121.69	121.79
O <sub>8</sub> ···H <sub>11</sub>	1.8676	1.7908
O <sub>8</sub> ···O <sub>10</sub>	2.6893	2.6745
O–H···O <sub>8</sub>	142.21	146.66
C=O···H <sub>11</sub>	99.19	98.77
energy (au)	–605.898 234 2	–607.606 350 1

<sup>a</sup> *r*<sub>e</sub> equilibrium bond lengths (Å) and angles (deg).

steps. The other formyl group was kept in the plane of the benzene ring. This approach permitted estimation of the barrier heights and some of the other parameters of the rotational potential energy functions. The interaction terms are canceled in this case. The results of these calculations along with the fitted rotational potential energy function (in the form of Fourier series),

$$V(\varphi_1, \varphi_2) = \frac{1}{2}V_1(2 - \cos \varphi_1 - \cos \varphi_2) + \frac{1}{2}V_2(2 - \cos 2\varphi_1 - \cos 2\varphi_2) + \frac{1}{2}V_3(2 - \cos 3\varphi_1 - \cos 3\varphi_2) + \frac{1}{2}V_4(2 - \cos 4\varphi_1 - \cos 4\varphi_2)$$

are shown in Figure 4. We obtained the following Fourier coefficients for 2,5-dihydroxyterephthalaldehyde,  $V_1 = 35.5$ ,  $V_2 = 42.9$ ,  $V_3 = 5.4$ ,  $V_4 = -0.5$ , and for 4,6-dihydroxyisophthalaldehyde,  $V_1 = 36.8$ ,  $V_2 = 62.9$ ,  $V_3 = 7.0$ ,  $V_4 = -1.0$  (all values in kJ/mol). The barrier height to internal rotation of the formyl

group in 4,6-dihydroxyisophthalaldehyde is calculated to be 85.0 kJ/mol at 95°, and that in 2,5-dihydroxyterephthalaldehyde is 63.7 kJ/mol at 100°.

## Structure Analysis

The electron diffraction structure analysis of 2,5-dihydroxyterephthalaldehyde was carried out by the least-squares fitting of calculated molecular scattering intensities to the experimental data, applying conventional single-start<sup>21</sup> and multistart Monte Carlo global optimization techniques.<sup>22</sup>

Initially the molecule was assumed to have  $C_{2h}$  symmetry, and its geometry was described by the following independent parameters.

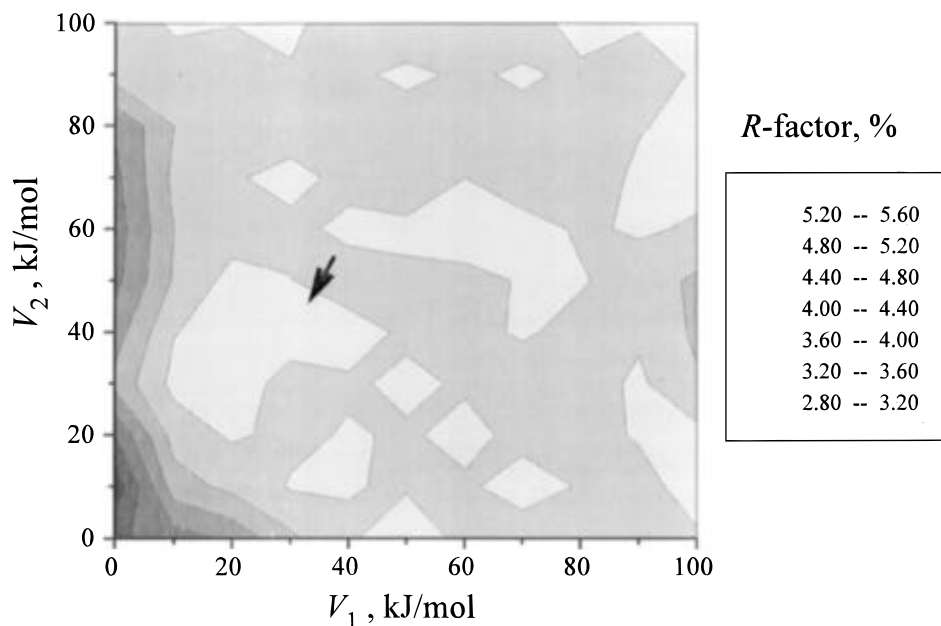
The benzene ring geometry was described by the mean value of the ring C–C bonds, two  $\Delta$ CC bond length differences (between C<sub>1</sub>–C<sub>2</sub> and C<sub>3</sub>–C<sub>4</sub>,  $\Delta$ CC1, and between C<sub>1</sub>–C<sub>2</sub> and C<sub>2</sub>–C<sub>3</sub>,  $\Delta$ CC2), and angles C<sub>1</sub>–C<sub>2</sub>–C<sub>3</sub> and C<sub>6</sub>–C<sub>1</sub>–C<sub>2</sub>. All C–H bonds of the benzene ring were assumed to have equal length and directed along the bisectors of the respective C–C–C angles. Following some initial attempts to refine the two  $\Delta$ CC differences independently, it was decided to assume these differences at the computed values. The choice of these assumed differences had no appreciable influence on the other parameters.

The geometry of the formyl group was described by the bond length differences between C<sub>1</sub>–C<sub>7</sub> and (C–C)<sub>mean</sub>,  $\Delta$ CC3; between C=O and (C–C)<sub>mean</sub>,  $\Delta$ CO; and between C<sub>7</sub>–H and (C–H)<sub>mean</sub> of the benzene ring,  $\Delta$ CH; by the angle C<sub>1</sub>–C<sub>7</sub>=O; and by the deviation of the direction of the C<sub>7</sub>–H bond from the bisector of the C<sub>1</sub>–C<sub>7</sub>=O angle,  $\Delta$ CCH. Varying the differences involving hydrogen atoms, i.e.,  $\Delta$ CH and  $\Delta$ CCH, has led to suspiciously large values. Thus these parameters were also assumed at the calculated ab initio values in the refinements throughout.

The hydroxy group was described with a  $\Delta$ CO bond length difference between C<sub>1</sub>–C<sub>2</sub> and C–O and with a  $\Delta$ OH difference between (C–H)<sub>mean</sub> and O–H. In addition, the C–O–H angle was refined as an independent parameter. The angle of torsion around the C–O bond could not be determined in the least-squares refinements, and it was assumed to be zero (allowing for the closest contact between the hydroxy group hydrogen and the formyl group oxygen), as suggested by the ab initio calculations.

Preliminary calculations, in which only one conformer of 2,5-dihydroxyterephthalaldehyde was considered, lead to a model with the C<sub>1</sub>–C<sub>7</sub> bond,  $r_a$ , 1.478(3), being the same as in benzaldehyde,  $r_a$ , 1.477(2).<sup>6</sup> Previous experience with similar intramolecular interactions in *o*-nitrophenols and the ab initio calculations both suggested this bond to be considerably shorter in 2,5-dihydroxyterephthalaldehyde than in benzaldehyde. Thus we performed Monte Carlo optimizations searching for a minimum in which certain conditions concerning the structural variations in 2,5-dihydroxyterephthalaldehyde as compared to benzaldehyde and phenol would be satisfied. The intramolecular motion of the formyl groups was described in terms of their rotational potential function in these calculations.

According to the estimations of parameters of the potential function describing the internal rotation of the formyl groups in 2,5-dihydroxyterephthalaldehyde and 4,6-dihydroxyisophthalaldehyde from ab initio calculations, the contribution of the first two terms in the Fourier series representation is essential. The rotational potential energy function for 2,5-dihydroxy-



**Figure 5.** Results of Monte Carlo optimization with different assumed values of the parameters of the potential energy function of internal rotation of the formyl groups in 2,5-dihydroxyterephthalaldehyde ( $V_1$  and  $V_2$ ) and initial geometries. The results are represented in the form of an  $R$ -factor map. The computed values (HF/6-31G\*, see text) are indicated by the arrow.

terephthalaldehyde was thus taken as

$$V(\phi_1, \phi_2) = \frac{1}{2}V_1(2 - \cos \phi_1 - \cos \phi_2) + \frac{1}{2}V_2(2 - \cos 2\phi_1 - \cos 2\phi_2)$$

in the electron diffraction structure analysis, ignoring higher order and interaction terms. Such an assumption may be reasonable because the higher order terms appear considerably smaller than these 1-fold and 2-fold terms in the results of the ab initio calculations. Interaction between well-separated formyl groups is supposed to be also small. The molecular model describing internal rotation of the formyl groups in 2,5-dihydroxyterephthalaldehyde included 91 rigid pseudoconformers with different  $\phi_1$  and  $\phi_2$  angles of formyl group torsion in the 0–180° interval with 15° steps. The other geometrical parameters were assumed to be the same in all conformers. The contribution of each pseudoconformer was calculated from a Boltzmann distribution with double statistical weights for conformers in which  $\phi_1 \neq \phi_2$ . The calculations were performed assuming different values of the parameters  $V_1$  and  $V_2$  in the 0–100 kJ/mol intervals using 200 different initial parameter sets in our Monte Carlo optimization. All other structure parameters and vibrational amplitudes were varied in these refinements. Results of the calculations in the form of the  $R$ -factor surface map as a function of  $V_1$  and  $V_2$  values are presented in Figure 5. The results indicate that there can be several models with different  $V_1$  and  $V_2$  values equally well approximating the experimental data, with one of these models corresponding to the computed ab initio parameters of the rotational potential function. Thus we assumed the  $V_1$  and  $V_2$  parameters at the calculated ab initio values in subsequent calculations.

Further Monte Carlo optimization with 200 initial geometries assuming the computed parameters of the rotational potential function has yielded a structure of 2,5-dihydroxyterephthalaldehyde that was consistent with the expected structural variations as compared to benzaldehyde and phenol on the basis of the ab initio calculations. The results are presented in Table 4. The standard deviations of model A were calculated in a special refinement in which all parameters were treated as variables,

**TABLE 4: Results of Electron Diffraction Least-Squares Refinements<sup>a</sup> of 2,5-Dihydroxyterephthalaldehyde**

parameter	model A <sup>b</sup>	parameter set B <sup>c</sup>
(C–C) <sub>mean</sub>	1.405(2)	1.404(3)
C <sub>1</sub> –C <sub>2</sub>	1.420(4)	1.418(3)
C <sub>2</sub> –C <sub>3</sub>	1.394(6)	1.392(3)
C <sub>3</sub> –C <sub>4</sub>	1.403(3)	1.401(3)
(C–H) <sub>mean</sub>	1.111(14)	1.111(16)
C <sub>6</sub> –C <sub>1</sub> –C <sub>2</sub>	121.2(5)	121.5(5)
C <sub>1</sub> –C <sub>2</sub> –C <sub>3</sub>	119.3(2)	118.7(3)
C <sub>2</sub> –C <sub>3</sub> –C <sub>4</sub>	119.5(7)	119.8(3)
C <sub>1</sub> –C <sub>7</sub>	1.466(3)	1.469(8)
C=O	1.229(1)	1.229(2)
C <sub>7</sub> –H <sub>9</sub>	1.128(16)	1.128(16)
C <sub>1</sub> –C <sub>7</sub> =O	124.6(4)	124.8(8)
C <sub>1</sub> –C <sub>7</sub> –H	116.0(10)	115.9(4)
C <sub>2</sub> –C <sub>1</sub> –C <sub>7</sub>	120.5(2)	120.2(5)
C–O	1.369(4)	1.370(4)
O–H	0.976(6)	0.974(5)
C <sub>1</sub> –C <sub>2</sub> –O	121.8(3)	122.8(5)
C–O–H	102.2(10)	101.0(12)
O <sub>8</sub> ···H <sub>11</sub> <sup>d</sup>	1.751(9)	1.765(8)
O <sub>8</sub> ···O <sub>10</sub> <sup>d</sup>	2.662(4)	2.677(8)
$R$ -factor, %	2.63	

<sup>a</sup>  $r_a$  distances (Å) and angles (deg) with least-squares standard deviations parenthesized in units of the last digit. <sup>b</sup> The least minimum from 200 refinements with different initial geometries. <sup>c</sup> Average structure using 200 parameter sets from the results of Monte Carlo optimization. The parenthesized standard deviations are calculated from these results and indicate the variations of the results as a consequence of choosing different initial parameters (bond lengths, bond angles, and amplitudes of vibrations), in reasonable intervals, in the refinements.

<sup>d</sup> All-planar hydrogen-bonded conformer.

except the parameters of the potential energy function. The parameter set B in the second column of Table 4 represents an average of the results from the Monte Carlo optimization. The parenthesized standard deviations are calculated from these results and indicate the variations of the results as a consequence of choosing different initial parameters (bond lengths, bond angles, and amplitudes of vibrations), in reasonable intervals, in the refinements. The larger standard deviations of the parameter set B, in some cases, as compared with those of model A, indicate the sensitivity of some of the bond lengths and bond angles to the choice of the initial values of the other parameters.

**TABLE 5: Bond Lengths ( $r_g$ , Å) and Bond Angles (deg) of 2,5-Dihydroxyterephthalaldehyde<sup>a</sup> with Estimated Total Errors from the Electron Diffraction Analysis Incorporating Constraints from ab Initio MO Calculations**

(C–C) <sub>mean</sub>	1.407 ± 0.004	C <sub>6</sub> –C <sub>1</sub> –C <sub>2</sub>	121.2 ± 0.7
C <sub>1</sub> –C <sub>2</sub>	1.422 ± 0.006	C <sub>1</sub> –C <sub>2</sub> –C <sub>3</sub>	119.3 ± 0.3
C <sub>2</sub> –C <sub>3</sub>	1.396 ± 0.009	C <sub>2</sub> –C <sub>3</sub> –C <sub>4</sub>	119.5 ± 1.0
C <sub>3</sub> –C <sub>4</sub>	1.405 ± 0.005	C <sub>2</sub> –C <sub>1</sub> –C <sub>7</sub>	120.5 ± 0.3
(C–H) <sub>mean</sub>	1.12 ± 0.02	C <sub>1</sub> –C <sub>7</sub> =O	124.6 ± 0.6
C <sub>1</sub> –C <sub>7</sub>	1.469 ± 0.005	C <sub>1</sub> –C <sub>7</sub> –H	116.0 ± 1.0
C=O	1.231 ± 0.003	C <sub>1</sub> –C <sub>2</sub> –O	121.8 ± 0.4
C <sub>7</sub> –H <sub>9</sub>	1.13 ± 0.02	C–O–H	102.2 ± 1.0
C–O	1.371 ± 0.006		
O–H	0.983 ± 0.009		

<sup>a</sup> Intramolecular motion of the formyl groups was treated in terms of their rotational potential function; see text.

## Results and Discussion

Bond lengths and bond angles from the joint electron diffraction/ab initio investigation of the molecular structure of 2,5-dihydroxyterephthalaldehyde with estimated total errors<sup>23</sup> are presented in Table 5. The results are compared with those of phenol and benzaldehyde in Tables 6 and 7, referring to the calculations and to electron diffraction, respectively. The parameters of salicylaldehyde are also listed for completeness.

**Benzene Ring Geometry.** The  $r_g(\text{C–C})_{\text{mean}}$  bond length of the benzene ring in 2,5-dihydroxyterephthalaldehyde, 1.407 ± 0.004 Å, shows a slight increase as compared with salicylaldehyde,<sup>6</sup> 1.404 ± 0.003 Å. This increase is within experimental error but may be better determined than it appears because both experiments may have the same systematic error which is the single largest component of the estimated total experimental error. The slight increase of the (C–C)<sub>mean</sub> bond length also appears in the results of the ab initio MP2(FC)/6-31G\* calculations on 2,5-dihydroxyterephthalaldehyde, 1.405 Å, as compared with salicylaldehyde,<sup>6</sup> 1.400 Å. An even larger difference is observed if compared with  $r_g(\text{C–C})_{\text{mean}}$  of some monosubstituted benzenes, such as benzaldehyde, 1.397 ± 0.003 Å from electron diffraction and 1.397 Å from ab initio MP2(FC)/6-31G\* calculations.<sup>6</sup> According to the ab initio MP2(FC)/6-31G\* calculations, the C–C bond between the substituents is considerably longer than the other C–C bonds in the benzene ring in both 2,5-dihydroxyterephthalaldehyde and 4,6-dihydroxyisophthalaldehyde (Tables 2 and 3). This is in agreement with the consequences of the intramolecular hydrogen bond formation observed for *o*-nitrophenols and contribution of *o*-quinonoid resonance forms of the molecules, presented in Scheme 2. Generally speaking, the notion of resonance-assisted

hydrogen bonding<sup>24</sup> has been a very useful concept in interpreting the structural variations in these compound series. It should be noted that the difference between the longest and the shortest C–C bond in the benzene ring is slightly larger in 4,6-dihydroxyisophthalaldehyde, 0.031 Å, than in 2,5-dihydroxyterephthalaldehyde, 0.026 Å. This may suggest a greater electron redistribution in the benzene ring of 4,6-dihydroxyisophthalaldehyde than in 2,5-dihydroxyterephthalaldehyde.

**Formyl Group Torsion.** The ab initio calculations indicated the existence of another stable conformer of 2,5-dihydroxyterephthalaldehyde and 4,6-dihydroxyisophthalaldehyde in which one of the formyl groups is being rotated to about 180° (Figure 4). However, their contribution at the experimental temperature should be small, as they have about 40 kJ/mol higher energy than the hydrogen-bonded conformers. Usually single-point ab initio calculations of the potential energy overestimate the absolute energy, while the difference between two barrier heights, calculated under the same conditions, may be free of such an error. The barrier height to internal rotation of the formyl groups in 2,5-dihydroxyterephthalaldehyde is 21.3 kJ/mol lower than that in 4,6-dihydroxyisophthalaldehyde. The present electron diffraction results concerning the internal rotation of the formyl groups in 2,5-dihydroxyterephthalaldehyde are in agreement with those from the ab initio calculations. The electron diffraction results are rather approximate in this respect (Figure 5).

**Intramolecular Hydrogen Bonding.** Some important structure parameters from the computations are compiled in Table 6. There is relatively strong intramolecular hydrogen bonding assisted by resonance in both molecules. This is inferred from the short O···H and O···O distances and from structural changes in the rest of the molecule, as compared with phenol and benzaldehyde. The shortening of the C<sub>1</sub>–CHO and C–O bonds and the lengthening of the C=O and O–H bonds as compared to the corresponding bonds in benzaldehyde and phenol are suggested by their resonance structures (Scheme 2). Note that changes in the C<sub>1</sub>–CHO, C–O, and O–H are more pronounced in 4,6-dihydroxyisophthalaldehyde than in 2,5-dihydroxyterephthalaldehyde.

An increase of the hydrogen bond strength in the series 2,5-dihydroxyterephthalaldehyde to salicylaldehyde to 4,6-dihydroxyisophthalaldehyde can be discerned in the calculated O···H/O···O distances: 1.815/2.687 Å, 1.803/2.681 Å, and 1.791/2.675 Å, respectively. The trend can also be seen in the changes of the other parameters; for example, the C–O, C<sub>1</sub>–CHO bonds shorten, the C(C)–C(O)–O, C–C(C)–C angles

**TABLE 6: Comparison of Some Important Geometrical Parameters<sup>a</sup> of Phenol, Benzaldehyde, 2,5-Dihydroxyterephthalaldehyde (I), Salicylaldehyde, and 4,6-Dihydroxyisophthalaldehyde (II) from ab Initio MP2(FC)/6-31G\* Calculations**

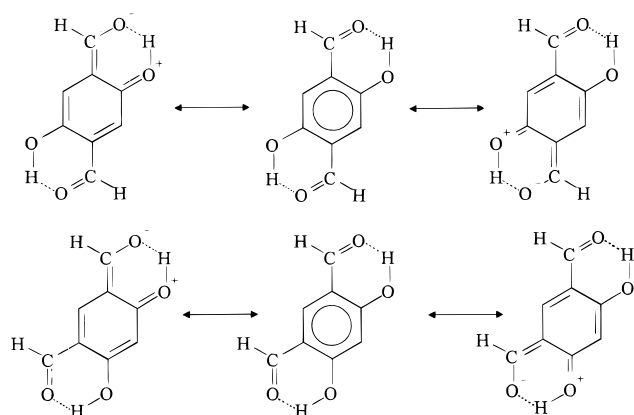
parameter	phenol <sup>b</sup>	benzaldehyde <sup>c</sup>	I	salicylaldehyde <sup>c</sup>	II	difference I – phenol	difference I – benzaldehyde	difference II – phenol	difference II – benzaldehyde
(C–C) <sub>mean</sub>	1.396	1.397	1.405	1.400	1.404	+0.009	+0.008	+0.008	+0.007
C <sub>1</sub> –C <sub>2</sub>	1.397	1.401	1.419	1.414	1.424	+0.022	+0.018	+0.027	+0.023
C–C(O)–C	120.3		118.5	119.3	120.3	–1.7		0.0	
C–C(C)–C		120.3	120.7	119.7	118.8		+0.4		–1.5
C <sub>1</sub> –C(=O)		1.480	1.465	1.460	1.457		–0.015		–0.023
C=O		1.227	1.239	1.240	1.240		+0.012		+0.013
C–C(C)–C(=O)		119.9	120.7	120.8	121.2		–0.8		–1.3
C–C=O		124.2	124.2	124.5	124.4		0.0		+0.2
C–O	1.375		1.354	1.353	1.346	–0.021		–0.029	
O–H	0.973		0.987	0.989	0.991	+0.015		+0.018	
C(C)–C(O)–O	122.8		123.1	122.7	121.8	+0.3		–1.0	
C–O–H	108.3		107.1	107.0	107.2	–1.2		–1.1	
O···H			1.815	1.803	1.791				
O···O			2.687	2.681	2.675				

<sup>a</sup>  $r_c$  distances (Å) and angles (degrees). <sup>b</sup> Reference 3. <sup>c</sup> Reference 6.

**TABLE 7: Comparison of Some Important Geometrical Parameters<sup>a</sup> of Phenol, Benzaldehyde, 2,5-Dihydroxyterephthalaldehyde (I), and Salicylaldehyde from Electron Diffraction**

parameter	phenol <sup>b</sup>	benzaldehyde <sup>c</sup>	I	salicylaldehyde <sup>c</sup>	difference I – phenol	difference I – benzaldehyde
(C–C) <sub>mean</sub>	1.399(3)	1.397(3)	1.407(4)	1.404(3)	+0.008	+0.010
C <sub>1</sub> –C <sub>2</sub>	1.399(3)	1.400(7)	1.422(6)	1.418(14)	+0.023	+0.022
C–C(O)–C	121.6(2)		119.3(3)	120.9(9)	–2.3	
C–C(C)–C		119.9(10)	121.2(7)	118.2(18)		+1.3
C <sub>1</sub> –C(=O)		1.479(4)	1.469(5)	1.462(11)		–0.10
C=O		1.212(3)	1.231(3)	1.225(4)		+0.019
C–C(C)–C(=O)		120.9(6)	120.5(3)	121.4(8)		–0.4
C–C=O		123.6(4)	124.6(6)	123.8(12)		+1.0
C–O	1.381(4)		1.371(6)	1.362(10)	–0.010	
O–H	0.958(3)		0.983(9)	0.985(14)	+0.025	
C(C)–C(O)–O	121.2(12)		121.8(4)	120.9(11)	+0.6	
C–O–H	106.4(17)		102.2(10)	104.8(26)	–4.2	
O···H			1.76(1)	1.74(2)		
O···O			2.667(8)	2.65(1)		

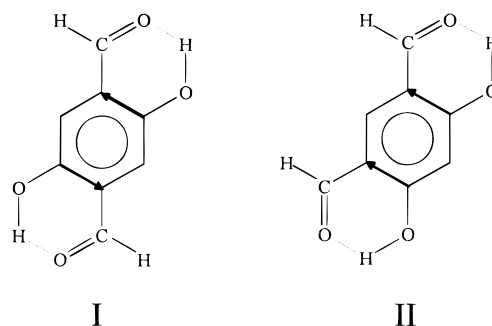
<sup>a</sup>  $r_g$  distances (Å) and  $r_a$  angles (degrees) with estimated total errors in the units of the last digit in parenthesis. <sup>b</sup> Reference 7. <sup>c</sup> Reference 6.

**SCHEME 2**

close, the C–C(C)–C angle opens, and the O–H bond lengthens in this series (Table 6). Increase of the barrier height to internal rotation in 4,6-dihydroxyisophthalaldehyde as compared to 2,5-dihydroxyterephthalaldehyde may also be an indication of stronger intramolecular interactions in 4,6-dihydroxyisophthalaldehyde.

The strength of the intramolecular hydrogen bonding seems affected by the mutual positioning of the interacting hydroxy and formyl groups in 2,5-dihydroxyterephthalaldehyde (I) and 4,6-dihydroxyisophthalaldehyde (II), just like it was recently observed in the computed structures of 2,5-dinitrohydroquinone and 4,6-dinitroresorcinol.<sup>10</sup> We suggest that the hydroxy group–formyl group interaction shifts the electron density from the hydroxy group toward the formyl group, and this shift is in direct relation with the intramolecular hydrogen bond formation. The mutual positioning of the two pairs of the interacting groups may increase this shift of electron density in 4,6-dihydroxyisophthalaldehyde because the directions of the shifts caused by each interacting pair coincide. This leads to greater electron redistribution and, consequently, stronger hydrogen bonding. In 2,5-dihydroxyterephthalaldehyde the shifts of the electron density, caused by each interacting pair of formyl and hydroxy group, would counteract each other, thus resulting in smaller overall electron density redistribution and, consequently, weaker intramolecular hydrogen bonding (Scheme 3).

The structural variations in 2,5-dihydroxyterephthalaldehyde from electron diffraction are consistent with those computed at the MP2(FC)/6-31G\* level (Table 7). There may also be a slight increase of the O···O distance in 2,5-dihydroxyterephthalaldehyde as compared with salicylaldehyde, but the experi-

**SCHEME 3**

mental errors are too large to draw any conclusion from this structural change.

**Conclusions**

1. There is resonance-assisted intramolecular hydrogen bonding in 2,5-dihydroxyterephthalaldehyde and 4,6-dihydroxyisophthalaldehyde. This implies not only short O···H and O···O distances but also considerable structural variations in both molecules comprising a shortening of the C–CHO and C–O bonds and a lengthening of the C=O, O–H bonds, and the C–C bond between the substituents in the benzene ring, as compared with the respective bonds in phenol and benzaldehyde.

2. Somewhat weaker intramolecular interactions can be discerned in 2,5-dihydroxyterephthalaldehyde than in 4,6-dihydroxyisophthalaldehyde as compared with parent molecules from the ab initio calculations. This may be attributed to the difference in the mutual positioning of the interacting pairs of the formyl and hydroxy groups.

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**Supporting Information Available:** Two tables showing total experimental electron diffraction intensities and background data (4 pages). Ordering information is given on any current masthead page.

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