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# Intramolecular Hydrogen Bonding and Molecular Structure of 2-Nitroresorcinol from Gas-Phase Electron Diffraction

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The molecular structure of 2-nitroresorcinol has been determined by electron diffraction in the gas phase. The formation of strong intramolecular hydrogen bonding between the nitro group oxygen and hydroxy hydrogen is indicated by the short H...O nonbonded distance,  $1.76 \pm 0.04$  Å. The O...O nonbonded distance (between the nitro and hydroxy groups),  $2.56 \pm 0.01$  Å, is also much shorter than twice the oxygen van der Waals radius. The hydrogen bond makes a  $110.5 \pm 1.5^\circ$  angle with the N=O bond corresponding to the direction where one of the oxygen lone pairs of electrons is anticipated. There are considerable bond length changes, as compared with nitrobenzene and phenol, consistent with strong resonance-assisted hydrogen bonding. In addition to the through-bond interactions connected with the H...O bond formation, angular changes suggest a through-space repulsive intersubstituent effect. The benzene ring geometry indicates a marked departure from additivity of individual substituent effects. The molecular geometry of 2-nitroresorcinol is characterized by the following bond lengths ( $r_g$ ) and bond angles: N=O,  $1.239 \pm 0.003$  Å; N—C,  $1.449 \pm 0.007$  Å; (C—C)<sub>mean</sub>,  $1.404 \pm 0.003$  Å; C<sub>1</sub>(N)—C<sub>2</sub>,  $1.426 \pm 0.005$  Å; C<sub>2</sub>—C<sub>3</sub>/C<sub>3</sub>—C<sub>4</sub>,  $1.393 \pm 0.004$  Å; (C—H)<sub>mean</sub>,  $1.090 \pm 0.015$  Å; C—O,  $1.354 \pm 0.004$  Å; O—H,  $1.038 \pm 0.015$  Å; O=N—O,  $121.4 \pm 0.5^\circ$ ; O=N—C,  $119.3 \pm 0.3^\circ$ ; N—C—C,  $120.5 \pm 0.4^\circ$ ; C<sub>1</sub>(N)—C<sub>2</sub>—O,  $122.8 \pm 0.7^\circ$ ; C—O—H,  $116 \pm 3^\circ$ ; C<sub>6</sub>—C<sub>1</sub>—C<sub>2</sub>,  $119.1 \pm 0.7^\circ$ ; C<sub>1</sub>—C<sub>2</sub>—C<sub>3</sub>,  $120.4 \pm 0.5^\circ$ ; C<sub>2</sub>—C<sub>3</sub>—C<sub>4</sub>,  $118.3 \pm 0.5^\circ$ ; C<sub>3</sub>—C<sub>4</sub>—C<sub>5</sub>,  $123.6 \pm 0.6^\circ$ .

## Introduction

Recently we have initiated a series of electron diffraction structure analyses, in which we are probing into possible intersubstituent effects in ortho-substituted benzene derivatives.<sup>1–3</sup> Thus, the molecular geometry of tetrafluorohydroquinone indicates possible formation of an intramolecular hydrogen bond between the OH and F substituents in ortho positions.<sup>1</sup> This is inferred not only from the short H...F distance,  $2.02 \pm 0.07$  Å, but also from other geometrical changes as compared with phenol<sup>4</sup> and hydroquinone.<sup>5</sup> These geometrical indications of intramolecular hydrogen bonding seem to diminish gradually from tetrafluorohydroquinone<sup>1</sup> to 2,6-difluorophenol<sup>2</sup> and to 2-fluorophenol<sup>2</sup> although relatively large experimental errors hinder a detailed comparison. In 2,6-difluorobenzenamine<sup>3</sup> and 2-fluorobenzenamine<sup>3</sup> no geometrical indications pointing to hydrogen bonding were detected except a slight tilt of the C—F bonds toward the amino group. All these electron diffraction studies have been facilitated by our earlier investigations of the molecular structure and ring deformation of substituted benzene derivatives (see, e.g., refs 6–8). Substituent impacts have been found to be generally additive if no substantial  $\pi$ -interactions are present between the substituents and the ring, while intersubstituent effects were absent in the non-ortho-substituted derivatives.

2-Nitroresorcinol was anticipated to be a suitable substance for intramolecular hydrogen bond formation as the expected H...O interaction is part of a six-membered ring. The above mentioned examples of fluorophenols and fluoroanilines have all represented cases in which the expected H...F interactions were part of a five-membered ring. Although accurate structures have been determined for nitrobenzene<sup>9</sup> and phenol,<sup>4</sup> the molecular geometry of 2-nitroresorcinol has not yet been investigated by either experimental or accurate computational techniques.<sup>10</sup>

## Experimental Section

A commercial Aldrich Chemie product served as sample<sup>11</sup> for the electron diffraction experiment in our modified EG-100A apparatus<sup>12a</sup> with a membrane nozzle system.<sup>12b</sup> Some of the

experimental conditions are summarized in Table I. The electron scattering factors were taken from available compilations.<sup>13</sup> The molecular intensities and radial distributions and models representing torsions and the numbering of atoms are shown in Figures 1–3.

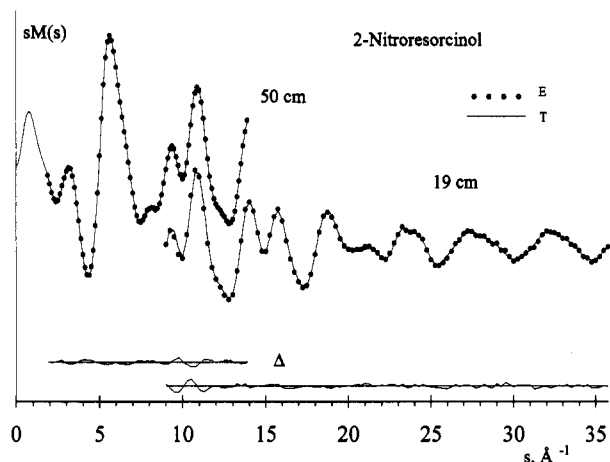
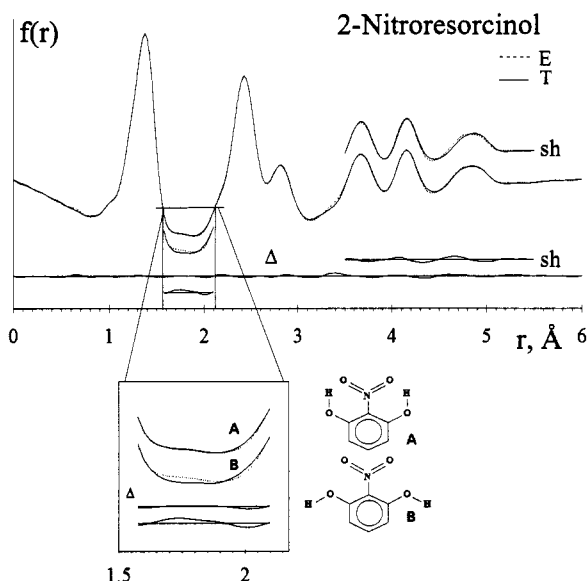
## Structure Analysis

The analysis was carried out by applying the least-squares method to the molecular intensities.<sup>14</sup> At the beginning the molecule was assumed to have  $C_{2v}$  symmetry except for the torsion of the nitro group. Supposing additivity in the changes of the intraring bond lengths, by considering the results on nitrobenzene<sup>9</sup> and phenol,<sup>4</sup> all the C—C bond lengths were anticipated to be the same within experimental error and only their mean value was included in the initial refinements. Also, at the beginning, O—H torsion from the ring plane has not been considered. Eventually, differences among ring C—C bond lengths and O—H torsion were added to the refinement as well as shrinkages of long nonbonded distances.

The geometry was finally described by bond lengths, bond length differences, bond angles, and angles of torsion, indicated as independent parameters in Table II, and three nonbonded distances were also treated as independent parameters. There was a direct indication of possible shrinkage effects at the 4.9 Å maximum on the radial distribution curve (Figure 2) as the experimental peak has consistently shown a shift toward smaller values, by a few hundredths of an angstrom, regardless of the conditions of refinement. The distances under this maximum are as follows C<sub>4</sub>...O<sub>15</sub>, C<sub>5</sub>...O<sub>15</sub>, and O<sub>7</sub>...O<sub>8</sub>. Subsequently, shorter distances, viz. those appearing under the maximum at 4.2 Å, and corresponding to similar arrangements as those under the 4.9 Å maximum have also been tested for possible shrinkage. Finally, only the nonbonded distances found to undergo appreciable shrinkage were varied as independent parameters. The inclusion of these nonbonded distances as independent variables in the refinement has improved the agreement between the experimental and calculated distributions while causing no substantial change in the resulting parameters.

TABLE I: Experimental Conditions for 2-Nitroresorcinol

no. of plates	camera dist (mm)	nozzle temp (°C)	wavelength (Å)	data intervals (Å <sup>-1</sup> )	data steps (Å <sup>-1</sup> )
7	500.4	142	0.04923	1.875–13.875	0.125
7	191.1	140	0.04923	9.00–35.75	0.25

Figure 1. Experimental (E) and theoretical (T) molecular intensities and their differences ( $\Delta$ ) for 2-nitroresorcinol.Figure 2. Experimental (E) and theoretical (T) radial distributions and the difference curve ( $\Delta$ ) for 2-nitroresorcinol. The separate portion (sh) between  $r = 3.5$  and  $5.5$  Å shows the appearance of possible shrinkage effects and the corresponding difference curve is also given (sh). The enlarged portion in the vicinity of  $r = 1.75$  Å demonstrates the discernible contribution of model A. Another pair of curves is shown for comparison where such a contribution is missing (model B).

The O–H torsion was assumed to have the same magnitude for the two hydroxy groups but the direction of torsion could be either the same or the opposite. Considering this in combination with the torsion of the nitro group, three different arrangements were possible as shown in Figure 3, corresponding to two short (A), two long (B), and one short/one long (C) H...O interactions. The best agreement was achieved for the coplanar A arrangement which allows the closest O...H nonbonded contacts indeed. However, the differences in *R*-factors are slight as the contributions involving the hydroxy hydrogens have relatively low weight in the total electron scattering. In fact, for this reason, electron diffraction is generally not very efficient for directly distinguishing among structures such as those represented in Figure 3 as the characteristic contributions are usually buried among contributions of much larger relative weight in the electron scattering. 2-Nitroresorcinol, however, has proved to be a rare favorable

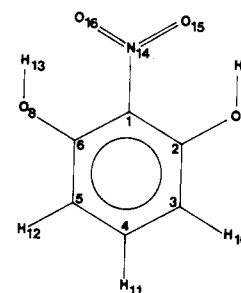
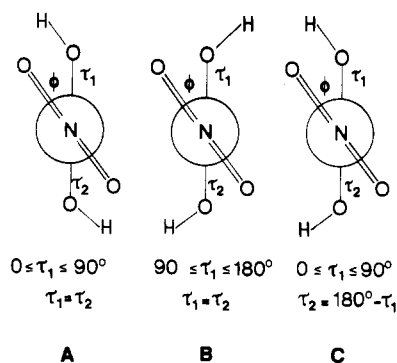


Figure 3. Molecular models representing torsions of the nitro and hydroxy groups and the numbering of atoms.

case in that there is a rather broad valley in the vicinity of  $1.75$  Å on the radial distribution curve (Figure 2) where the contribution of the shortest H...O nonbonded distance is expected to appear. There is a small hump at around  $1.75$  Å on the experimental radial distribution which gains real significance when it is compared with the calculated distributions. The curve of model A shows evidence of some small contribution at  $1.75$  Å which is absent in the curve of model B.<sup>15</sup> Unfortunately, the angles of torsion about the C–N and the C–O bonds could not be refined in the least-squares calculations.

Only a mean value was refined for the ring C–C bond lengths until the last stages of the analysis. However, the resonance structures shown in Scheme I would correspond to a split in the C–C bond lengths, making those between the substituents somewhat longer and the others somewhat shorter. The refinements allowing for C–C bond length differences have always moved to increase the C<sub>1</sub>–C<sub>2</sub> bond length and decrease C<sub>2</sub>–C<sub>3</sub> and C<sub>3</sub>–C<sub>4</sub>. Distinguishing between C<sub>2</sub>–C<sub>3</sub> and C<sub>3</sub>–C<sub>4</sub> did not lead to improvement of the refinement.

Concerning the mean amplitudes of vibration (*l*), they were grouped together according to the appearance of the corresponding contributions on the radial distribution. The differences among the *l*-values within the same group belonging to the same maximum were kept fixed in a given refinement. The grouping of the amplitudes is indicated in Table II. We have tested the influence of assumptions of the fixed differences among the amplitudes and found that it did not exceed experimental errors.

A representative set of results of the least-squares refinements is given in Table II. This set is representative only because there may be many variations in the conditions of refinement; however, this set can also be considered the final results as the important parameters have proved to be insensitive to changes in the refinement conditions, compared with experimental errors. Table III lists the elements of the correlation matrix with absolute value greater than 0.6; there are remarkably few such elements.

## Results and Discussion

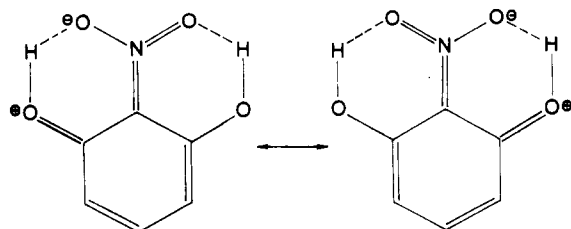
The bond lengths ( $r_b$ ) and bond angles with estimated total errors<sup>16</sup> are listed in Table IV.

TABLE II: Results of Least-Squares Refinement<sup>a</sup> of 2-Nitroresorcinol

type	$r_a$	$l$	groups	type	$r_a$	$l$	groups
Independent Parameters							
(C-C) <sub>mean</sub>	1.4022 (7)			$\Delta CC1^c$	0.034 (4)		
(C-H) <sub>mean</sub>	1.085 (10)	0.078 (1)	i	$\Delta CC2^c$	0.034		
$\angle C_6-C_1-C_2$	119.1 (5)			$\Delta CO^c$	0.050 (3)		
$\angle C_1-C_2-C_3$	120.4 (3)			$\Delta OH^c$	0.052 (18)		
$\angle C_1-C_2-O_7$	122.8 (4)			$\Delta CN^c$	0.045 (5)		
$\angle C_4-C_3-H_{10}$	122.1 (34)			$\Delta NO^c$	0.165 (1)		
$\angle C_1-N_{14}-O_{15}$	119.3 (2)			$C_3 \cdots C_{16}$	4.711 (7)	0.076 (6)	ii
$\angle C_2-O_7-H_9$	115.9 (24)			$O_7 \cdots O_8$	4.831 (10)	0.078	ii
$\tau_1^b$	0.0 (fixed)			$C_3 \cdots O_8$	4.145 (6)	0.065 (2)	iii
$\phi^b$	0.0 (fixed)						
Dependent Distances and Angles							
$O_7-H_9$	1.032 (10)	0.080	i	$N_{14} \cdots H_{10}$	4.636 (35)	0.127	ii
$C_1-C_2$	1.425 (3)	0.049	i	$N_{14} \cdots H_{11}$	5.302 (11)	0.122	ii
$C_2-C_3$	1.391 (2)	0.049	i	$O_7 \cdots H_{10}$	2.553 (61)	0.148	iv
$C_3-C_4$	1.391 (2)	0.049	i	$O_7 \cdots H_{11}$	4.465 (10)	0.135	ii
$C_2-O_7$	1.353 (2)	0.046	i	$O_7 \cdots H_{12}$	5.257 (12)	0.113	ii
$C_1-N_{14}$	1.448 (5)	0.052	i	$O_7 \cdots H_{13}$	4.964 (40)	0.120	ii
$N_{14}-O_{15}$	1.238 (1)	0.043	i	$O_{15} \cdots H_9$	1.755 (29)	0.133	i
$C_1 \cdots C_4$	2.770 (6)	0.0598	fixed	$O_{15} \cdots H_{10}$	4.828 (48)	0.166	ii
$C_2 \cdots C_5$	2.821 (3)	0.0598	fixed	$O_{15} \cdots H_{11}$	6.005 (12)	0.099 (40)	vii
$C_2 \cdots C_6$	2.457 (5)	0.055 (2)	iv	$O_{15} \cdots H_{12}$	5.716 (29)	0.099	vii
$C_2 \cdots C_4$	2.388 (4)	0.055	iv	$O_{15} \cdots H_{13}$	3.678 (39)	0.172	v
$C_1 \cdots C_3$	2.443 (5)	0.055	iv	$C_1 \cdots H_{10}$	3.424 (25)	0.116	v
$C_3 \cdots C_5$	2.452 (5)	0.055	iv	$C_1 \cdots H_{11}$	3.854 (12)	0.119	v
$C_1 \cdots O_7$	2.438 (3)	0.060	iv	$C_1 \cdots H_9$	2.589 (40)	0.154	iv
$C_1 \cdots O_{15}$	2.319 (4)	0.066	iv	$C_2 \cdots H_{10}$	2.145 (37)	0.114	iv
$C_2 \cdots O_8$	3.714 (4)	0.069 (3)	v	$C_2 \cdots H_{11}$	3.365 (10)	0.116	v
$C_2 \cdots O_{15}$	2.779 (4)	0.100 (4)	vi	$C_2 \cdots H_{12}$	3.906 (11)	0.116	iii
$C_2 \cdots O_{16}$	3.609 (3)	0.082	v	$C_2 \cdots H_9$	2.028 (28)	0.113	iv
$C_3 \cdots O_7$	2.338 (4)	0.062	iv	$C_2 \cdots H_{13}$	4.000 (38)	0.136	iii
$C_3 \cdots O_8$	4.173 (3)			$C_3 \cdots H_{11}$	2.130 (9)	0.114	iv
$C_3 \cdots O_{15}$	4.168 (4)	0.098	iii	$C_3 \cdots H_{12}$	3.436 (27)	0.116	v
$C_3 \cdots O_{16}$	4.761 (4)			$C_3 \cdots H_9$	3.259 (21)	0.117	v
$C_4 \cdots O_7$	3.605 (3)	0.070	v	$C_3 \cdots H_{13}$	4.742 (35)	0.158	ii
$C_4 \cdots O_{15}$	4.942 (5)	0.077	ii	$C_4 \cdots H_{10}$	2.171 (38)	0.114	iv
$C_2 \cdots N_{14}$	2.493 (4)	0.059	iv	$C_4 \cdots H_9$	4.412 (26)	0.123	iii
$C_3 \cdots N_{14}$	3.766 (4)	0.072	v	$\angle N-C_1-C_2$	120.5 (2)		
$C_4 \cdots N_{14}$	4.217 (6)	0.075	iii	$\angle C_2-C_3-C_4$	118.3 (3)		
$N_{14} \cdots O_7$	2.892 (5)	0.093	vi	$\angle C_3-C_4-C_5$	123.6 (4)		
$O_7 \cdots O_8$	4.871 (7)			$\angle O_{15}-N_{14}-O_{16}$	121.4 (3)		
$O_7 \cdots O_{15}$	2.554 (6)	0.102	iv	$C-O$ , tilt <sup>d</sup>	2.9 (3)		
$O_7 \cdots O_{16}$	4.128 (5)	0.097	iii	$\angle O_7-H_9 \cdots O_{15}^e$	131.1 (32)		
$O_{15} \cdots O_{16}$	2.159 (3)	0.053	iv	$\angle H_9 \cdots O_{15}=N_{14}^f$	110.5 (10)		
$N_{14} \cdots H_9$	2.476 (39)	0.165	iv	R-factor	3.82		

<sup>a</sup> Least-squares standard deviations are parenthesized in units of the last digit. <sup>b</sup> Angles of torsion, see Figure 3. <sup>c</sup>  $\Delta CC1 = r(C_1-C_2) - r(C_2-C_3)$ ,  $\Delta CC2 = r(C_1-C_2) - r(C_3-C_4)$ ,  $\Delta CO = r(C-C)_{\text{mean}} - r(C-O)$ ,  $\Delta OH = r(C-H)_{\text{mean}} - r(O-H)$ ,  $\Delta CN = r(C-N) - r(C-C)_{\text{mean}}$ ,  $\Delta NO = r(C-C)_{\text{mean}} - r(N=O)$ . <sup>d</sup> Positive when tilt is away from the hydrogen bond. <sup>e</sup> Angle made by the H-O bond and the hydrogen bond. <sup>f</sup> Angle made by the hydrogen bond and the N=O bond.

## SCHEME I



**Nitro Group Torsion.** The nitro group appears coplanar with the benzene ring. Nitrobenzene itself was found to be coplanar by microwave spectroscopy,<sup>17</sup> whereas its electron diffraction analysis<sup>9</sup> yielded an angle of torsion  $13.3 \pm 1.4^\circ$ . This was, however, considered to be an operational effect resulting from torsional vibrations. Assuming a simple potential function of the form  $V(\phi) = (V_2/2)(1 - \cos 2\phi)$ , the barrier to rotation of the nitro group,  $V_2$ , was estimated<sup>18</sup> from the angle of torsion to be around 17 kJ mol<sup>-1</sup>. The angle of torsion could not be refined in 2-nitroresorcinol; however, the planar or close-to-planar structure, consistent with the electron diffraction data, suggests a much higher barrier to torsion than that of nitrobenzene. The nitro torsion of 2-nitroresorcinol may be governed by a rather flat

TABLE III: Correlation Matrix Elements with Absolute Values Greater than 0.6 for 2-Nitroresorcinol

$i$	$j$	$x_{ij}$
$r(C-C)_{\text{mean}}$	$\Delta CO$	0.6834
$\Delta CC1$	$\angle C-C_1-C$	-0.6840
	$\angle C_1-C_2-O$	-0.7460
$\angle C-C_1-C$	$\angle C-C_2-C$	-0.8721
	$\angle C_1-C_2-O$	0.7114
$\angle C-C_2-C$	$\angle C_1-C_2-O$	0.8359
$r(C-H)_{\text{mean}}$	$\Delta OH$	0.8705
$\Delta CO$	$\Delta NO$	0.6486
$\Delta CN$	$\angle C-N=O$	-0.6055

but not wide well of the potential energy function in the vicinity of the minimum-energy coplanar conformation. The higher torsional barrier of 2-nitroresorcinol as compared with nitrobenzene is probably caused by the restraining influence of the hydrogen bonds, whereas no such bonds are present in nitrobenzene.

**Intramolecular Hydrogen Bonding.** The discernible contribution from model A to the experimental radial distribution in the vicinity of 1.75 Å provides direct evidence for a relatively short hydrogen bond.<sup>19</sup> It is a fortunate coincidence that a relatively small region on the experimental radial distribution can be

**TABLE IV: Bond Lengths ( $r_e$ , Å) and Bond Angles (deg) of 2-Nitroresorcinol<sup>a</sup> with Estimated Total Errors<sup>b</sup>**

N=O	1.239 ± 0.003	O=N=O	121.4 ± 0.5
N—C	1.449 ± 0.007	O=N—C	119.3 ± 0.3
C—O	1.354 ± 0.004	N—C <sub>1</sub> —C <sub>2</sub>	120.5 ± 0.4
O—H	1.038 ± 0.015	C <sub>1</sub> —C <sub>2</sub> —O	122.8 ± 0.7
(C—C) <sub>mean</sub>	1.404 ± 0.003	C—O—H	116 ± 3
C <sub>1</sub> —C <sub>2</sub>	1.426 ± 0.005	C <sub>6</sub> —C <sub>1</sub> —C <sub>2</sub>	119.1 ± 0.7
C <sub>2</sub> —C <sub>3</sub> /C <sub>3</sub> —C <sub>4</sub>	1.393 ± 0.004	C <sub>1</sub> —C <sub>2</sub> —C <sub>3</sub>	120.4 ± 0.5
(C—H) <sub>mean</sub>	1.090 ± 0.015	C <sub>2</sub> —C <sub>3</sub> —C <sub>4</sub>	118.3 ± 0.5
		C <sub>3</sub> —C <sub>4</sub> —C <sub>5</sub>	123.6 ± 0.6

<sup>a</sup> All-planar model. <sup>b</sup> They include an 0.2% experimental scale error and 2<sup>1/2</sup> times the least-squares standard deviation.<sup>16</sup>

**TABLE V: Structural Parameters<sup>a</sup> Indicating Intersubstituent Interactions in 2-Nitroresorcinol and Parameters in Other Systems for Comparison**

	2-nitroresorcinol	other systems <sup>b</sup>	
H...O, Å	1.76 ± 0.4	ΣvdW, Å	2.60
O...O(O—H...O), Å	2.558 ± 0.010	ΣCov, Å	0.977
		ΣvdW, Å	2.80
N=O, Å	1.239 ± 0.003	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	1.223 ± 0.003
N—C, Å	1.449 ± 0.007	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	1.486 ± 0.004
C <sub>1</sub> —C <sub>2</sub> , Å	1.426 ± 0.005	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> and C <sub>6</sub> H <sub>5</sub> OH (mean)	1.399 ± 0.003
C—O, Å	1.354 ± 0.004	C <sub>6</sub> H <sub>5</sub> OH	1.381 ± 0.004
O—H, Å	1.038 ± 0.015	C <sub>6</sub> H <sub>5</sub> OH	0.958 ± 0.003
H...O=N, <sup>c</sup> deg	110.5 ± 1.5		
O—H...O, <sup>d</sup> deg	131 ± 5		
O=N—C, <sup>e</sup> deg	119.3 ± 0.3	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	117.3 ± 0.1
C—O tilt, <sup>e</sup> deg	2.9 ± 0.5	C <sub>6</sub> H <sub>5</sub> OH	2
C—O—H, <sup>e</sup> deg	116 ± 3	C <sub>6</sub> H <sub>5</sub> OH	106.4 ± 1.7

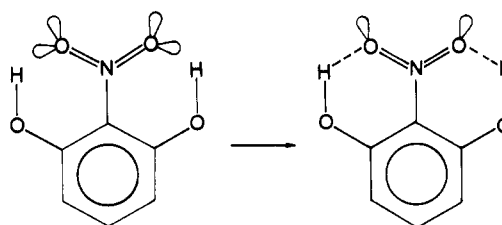
<sup>a</sup> Bond lengths are  $r_e$ . <sup>b</sup> ΣvdW means the sum of van der Waals radii; ΣCov means the sum of covalent radii; C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>, nitrobenzene; C<sub>6</sub>H<sub>5</sub>OH, phenol.<sup>4</sup> <sup>c</sup> The angle made by the hydrogen bond and the adjacent N=O bond. <sup>d</sup> The angle made by the hydrogen bond and the O—H bond. <sup>e</sup> The C—O tilt is positive when bending away from the hydrogen bond.

assigned to the contribution from the hydrogen bond. However, there is considerable additional evidence for the presence of this hydrogen bond among the geometrical data on 2-nitroresorcinol. Structural parameters indicating geometrical consequences of the hydrogen bond formation are collected in Table V. Even though there is a large experimental error associated with the H...O distance, 1.76 ± 0.04 Å, it is about midway (1.79 Å) between the sums of covalent radii and van der Waals radii. The distance between the two oxygen atoms involved in this hydrogen bond as bridgeheads provides additional evidence for the hydrogen bond, and it is determined with considerably greater precision than the H...O distance.

The N=O bond is longer and the N—C bond is shorter in 2-nitroresorcinol than in nitrobenzene, whereas the C—O bond is shorter and the O—H bond is longer in 2-nitroresorcinol than in phenol. All this is in excellent agreement with the expected consequences of hydrogen bond formation. Similar bond length changes have been observed in the dimers of carboxylic acids, due to hydrogen bond formation, as compared with the structures of their monomers.<sup>20</sup>

The C<sub>1</sub>—C<sub>2</sub> bond in the benzene ring is in between the two substituents and it is also part of the six-membered ring that contains the hydrogen bond. Its considerable lengthening is in accordance with the resonance structures of Scheme I. Resonance-assisted hydrogen bonding, both intramolecular and intermolecular, has been described for a number of crystal molecular structures,<sup>21</sup> whereas 2-nitroresorcinol represents an example of a free molecule in the gaseous state.

The two angles involving the hydrogen bond itself are of special interest. For the angle H...O=N, made by the hydrogen bond and the adjacent N=O bond, the ideal value would have the H...O interaction coincide with the direction of the nearest lone

**SCHEME II**

pair of electrons, as suggested by the VSEPR model.<sup>22</sup> This is illustrated in Scheme II. Considering the oxygen of the nitro group to be the central atom, it may be described as N=O<sub>2</sub>, i.e., having one bond domain and two lone pairs. They will have a planar triangular arrangement and ideally 120° angles between the charge centroids of the electron domains. The 110.5 ± 1.5° angle may indicate a larger-than-120° angle between the two lone pairs, supposed to be due to the greater space requirement of a lone pair domain than that of the N=O bond domain. The O—H...O angle, 131 ± 5°, made by the hydrogen bond and the H—O bond is considerably larger than the 120° of a regular hexagon but much smaller than 180° of the ideal O—H...O arrangement.

Four further bond angles characterize the six-membered ring that includes the hydrogen bond (Table IV). All of them are larger than the corresponding angles, ONC 117.3 ± 0.1 and NCC 118.3 ± 0.3° in nitrobenzene<sup>9</sup> and CCO 121.2 ± 1.2° and COH 106 ± 4°, in phenol.<sup>4</sup> Thus there seems to be a repulsive intersubstituent effect between the nitro and hydroxy groups tending to expand the bond angles.<sup>23</sup> This may be supposed to be a ligand/ligand repulsion, i.e. a through-space interaction, manifested in angular openings. The attractive hydrogen bonding interaction, on the other hand, is a through-bond interaction causing bond lengthenings and shortenings.

A recent semiempirical study<sup>24</sup> of 2-nitrophenol, including a small-basis ab initio calculation, and earlier X-ray crystallographic investigations of 2-nitrophenol and several of its derivatives<sup>25</sup> have also shown intramolecular hydrogen bonding and the respective O...O nonbonded distances similar to those found in 2-nitroresorcinol. The bond length and bond angle variations in crystal-phase 2-nitrophenols demonstrate similar effects to those discussed above. Because of the different physical meanings, direct comparison of these parameters, especially the bond lengths, with those of the gas electron diffraction geometry of 2-nitroresorcinol has rather limited value. However, it is of interest to mention that the N=O bond participating in the hydrogen bond is typically longer than the other N=O bond by several hundredths of an angstrom, and the C<sub>1</sub>—C<sub>2</sub> bond in the ring, in between the O—H and NO<sub>2</sub> substituents, is also longer than the adjacent C—C bond in the ring though to varying extent. The H...O=N and O—H...O angles are around 105 and 135°, respectively.<sup>26</sup> In contrast to the crystallographic results on 2-nitrophenols, a microwave spectroscopic investigation<sup>27</sup> of gaseous 2-nitrophenol itself established no marked structural change due to the strong hydrogen bond. However, there was not enough data for a complete structure determination.

**Benzene Ring Geometry.** The mean value of the CC bond length in the benzene ring of 2-nitroresorcinol is determined with high precision. It appears somewhat larger than that in nitrobenzene<sup>9</sup> and in phenol,<sup>4</sup> both 1.399 ± 0.003 Å, but the difference is within experimental error.<sup>28</sup> The mean C—H bond length is in good agreement with those in nitrobenzene,<sup>9</sup> 1.093 ± 0.004 Å, and phenol,<sup>4</sup> 1.086 ± 0.003 Å. Concerning the angular deformation, there is a marked departure from additivity of substituent impact. The ring angles of 2-nitroresorcinol can be calculated assuming additivity from the electron diffraction structures of gaseous nitrobenzene<sup>9</sup> and phenol<sup>4</sup> (1) and from the angular substituent parameters in the solid state (2),<sup>8</sup> and the

following values are obtained (1/2): C<sub>6</sub>C<sub>1</sub>C<sub>2</sub>, 121.0/122.1°; C<sub>1</sub>C<sub>2</sub>C<sub>3</sub>, 119.9/118.9°; C<sub>2</sub>C<sub>3</sub>C<sub>4</sub>, 119.0/119.3°; C<sub>3</sub>C<sub>4</sub>C<sub>5</sub>, 121.4/121.6°. The calculated patterns 1 and 2 seem to be characteristic while their internal consistency is not very good. However, the geometry of 2-nitroresorcinol demonstrates strong intersubstituent effects and thus additivity should break down, and it does. There is also considerable bond length change in the ring, much larger than the usual individual substituent effects. The bond length changes seem to be determined by the resonance structures of Scheme I.

## Conclusions

1. There is strong, resonance-assisted intramolecular hydrogen bonding in 2-nitroresorcinol.
2. Nitro-group torsion is hindered by considerably higher barrier in 2-nitroresorcinol than in nitrobenzene.
3. The geometrical consequences of the attractive through-bond and the repulsive through-space interactions seem to appear well separated, at least as a good approximation, in bond length changes and angular changes, respectively, as compared with the structures of nitrobenzene and phenol.
4. Gas-phase electron diffraction is a suitable technique to investigate intramolecular intersubstituent effects, especially in relatively symmetrical molecules. 2-Nitroresorcinol has proved to be a fortunate subject for detecting intramolecular hydrogen bonding.

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**Supplementary Material 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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