Intramolecular Hydrogen Bonding and Molecular Geometry of 4,6-Dinitroresorcinol from Gas-Phase Electron Diffraction

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The molecular geometry of 4,6-dinitroresorcinol has been determined by gas-phase electron diffraction. The resonance-assisted intramolecular hydrogen bonding is accompanied by pronounced bond length changes as compared with the parent molecules phenol and nitrobenzene. The molecular geometry is characterized by the following bond lengths (r_g) and bond angles: (C-H)_{mean}, 1.086 ± 0.015 Å; (C-C)_{mean}, 1.402 ± 0.003 Å; C₃-C₄, 1.424 ± 0.005 Å; C-O, 1.341 ± 0.004 Å; O-H, 1.002 ± 0.009 Å; C-N, 1.461 ± 0.004 Å; (N-O)_{mean}, 1.233 ± 0.003 Å; ∠C₁-C₂-C₃, 120.3 ± 0.4°; ∠C₂-C₃-C₄, 119.3 ± 0.3°; ∠C₃-C₄-C₅, 121.6 ± 0.3°; ∠C₄-C₅-C₆, 118.0 ± 0.4°; ∠C₄-C₃-O, 123.4 ± 0.3°; ∠C-O-H, 104.5 ± 1.4°; ∠C₃-C₄-N, 121.0 ± 0.2°; (∠C-N-O)_{mean}, 118.1 ± 0.1°; ∠O-N-O, 123.7 ± 0.2°. The effective angle of nitro group torsion from electron diffraction is 14.4 ± 1.3°. If it is assumed that this effective angle of torsion emerges as a consequence of torsional vibrations about the planar equilibrium conformation, then a barrier to internal rotation of 18 ± 3 kJ/mol may be estimated, the same as in nitrobenzene, the planarity of which is consistent with microwave spectroscopic results.

Introduction

Our recent investigations of the molecular structures of 2-nitrophenol² and 2-nitroresorcinol^{3,4} determined the presence of considerable intramolecular hydrogen bonding in these molecules. Appreciable geometrical changes were observed as compared to the structures of phenol⁵ and nitrobenzene.⁶ The angular changes in the benzene ring of 2-nitrophenol and 2-nitroresorcinol were different from those predicted by supposing additivity of the angular distortions from phenol and nitrobenzene.⁷ The influence of the substituents, involved in the resonance-assisted intramolecular hydrogen bonding,⁸ on the rest of the molecule does not seem to follow additivity of their independent contributions. On the other hand, it seems important to investigate the influence of pair wise interacting substituents. From the point of view of the electron diffraction technique, such derivatives are quite favorable since many of the interactions of interest double, giving hope for a more accurate determination of the related structural features. As a continuation of our research into ortho-substituted benzene derivatives, we are reporting here the electron diffraction investigation of the molecular structure of 4,6-dinitroresorcinol (Figure 1).

Experimental Section

Synthesis. 1,3-Diacetoxybenzene. 1,3-Diacetoxybenzene was obtained by reaction of resorcinol with acetyl chloride. The mixture of 20 g (0.18 mol) resorcinol with 30 mL (33.15 g, 0.42 mol) acetyl chloride was left at room temperature for 4 h until a transparent solution formed. Then it was boiled under reflux for 3 h and fractionated at atmospheric pressure. A sample of 32.60 g (92.4%) of pale yellow liquid was obtained, bp 278-282 °C (literature⁹ bp 278 °C).

4,6-Dinitroresorcinol. 4,6-Dinitroresorcinol was obtained by nitration of 1,3-diacetoxybenzene and by the following hydrolysis of 1,3-diacetoxy-4,6-dinitrobenzene. A sample of 85 mL (1.49 mol) of 77% nitric acid ($d_{20} = 1.44$) was cooled in an ice bath. Then 28.70 g (0.147 mol) of 1,3-diacetoxybenzene was



Figure 1. Numbering of atoms for 4,6-dinitroresorcinol.

dropped into the acid within 1-2 min with stirring. The mixture was then stirred for 80 min and diluted with ice cool water following extraction by ether $(4 \times 100 \text{ mL})$ at room temperature. The solvent from combined organic phases was then removed under reduced pressure, and 20 mL of water and 30 mL of saturated hydrochloric acid were added to the resulting product for the hydrolysis. The mixture was heated for 3 h in a water bath and left for 48 h at room temperature. After addition of 200 mL of water a brown-yellow precipitate was obtained. The precipitate was filtered, washed with 60 mL water, and purified by the following procedure. It was mixed with 100 mL of water and heated until the mixture boiled, and the insoluble part (4,6dinitroresorcinol) was filtered. After this procedure had been performed twice, the precipitate was recrystallized from ethyl acetate, dried, and then sublimated in vacuum (0.1 Torr) in an oil bath at 145 °C, yielding 4.14 g (14%) of the product, mp 217-218 °C (literature⁹ mp 215 °C). The purity of the product was checked by thin layer chromatography.

Electron Diffraction Experiment. The electron diffraction photographs were recorded in our modified EG-100A apparatus¹⁰ with a membrane nozzle system¹¹ from two nozzle-to-plate distances. Some of the experimental conditions are summarized in Table 1. The atomic electron-scattering factors were taken from available compilations.¹² The experimental and theoretical molecular intensities and radial distributions are shown in Figures 2 and 3. The numbering of atoms is presented in Figure 1.

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TABLE 1: Experimental Conditions for 4,6-Dinitroresorcinol



Figure 2. Experimental (E) and theoretical (T) molecular intensities and twice their differences (2Δ) for 4,6-dinitroresorcinol.

25

35

30

10 15 20

0 5



Figure 3. Experimental (E) and theoretical (T) radial distributions and twice their differences (2Δ) for 4,6-dinitroresorcinol.

Structure Analysis. The analysis was carried out by the least-squares method, using the molecular intensities.¹³ Initially, the molecule was assumed to have $C_{2\nu}$ symmetry, with the 2-fold axis passing through the two unsubstituted carbon atoms. This symmetry was lowered when torsion of the substituent groups was investigated.

The geometry of the nitro groups was described by the ΔNO bond length difference between the $(C-C)_{mean}$ and one of the N-O bonds, by the $\Delta NO2$ bond length difference between the two N-O bonds in the same group, as well as by the $(C-N-O)_{mean}$ angle, and by the difference between the two C-N-O angles in the same group. Varying these differences as independent parameters, or fixing them stepwise at different reasonable values, has shown no appreciable influence on the other parameters. The $\Delta NO2$ and ΔCNO differences were further assumed to be equal to those obtained in the structural analysis of 2-nitrophenol.²

The possibility of nitro group torsion was further examined assuming the torsional angle to be equal for the two nitro groups. As a consequence of such torsional vibrations, the overall symmetry of the model reduces to C_s or C_2 , depending on the mutual direction of the torsion of the two nitro groups. Introduction of such a parameter into the refinement improved the general agreement but did not appreciably influence the other parameters. The angle of the nitro group torsion has been refined to 14.4(9)°. Refinements of the models possessing C_s or C_2 symmetry have indicated no difference, beyond the experimental errors, between the parameters, including the angles of rotation. On the basis of the electron diffraction data alone it is not possible to distinguish between a planar model with relatively large-amplitude torsional vibrations and a nonplanar model (see also in the discussion).

The hydroxy groups were described by the ΔCO difference between the $(C-C)_{mean}$ and the C-O bond lengths, by the ΔOH





difference between the $(C-H)_{mean}$ and the O-H bond lengths, and by the C-O-H bond angle. The angle of torsion around the C-O bond was assumed to be zero when the hydroxy group was located in the plane of the benzene ring and turned toward the nitro group. This conformation, allowing the closest contact between the substituents, proved to be the most preferable in the joint ab initio and electron diffraction study of 2-nitrophenol.²

The benzene ring geometry was described by the mean value of the ring C-C bonds and two Δ CC bond length differences (between C_3-C_4 and C_2-C_3 and between C_3-C_4 and C_4-C_5), as well as by two C-C-C angles at the nitro and the hydroxy groups. All the C-H bonds were assumed to have equal length and directed along the bisectors of the respective C-C-Cangles. Initially, the two ΔCC bond length differences were refined independently. Eventually, however, as the difference between them, obtained from the least-squares refinements, appeared smaller than their standard deviations, they were assumed to be equal. The assumption that the C_2-C_3 and C_4- C₅ bond lengths are equal had no influence on the other parameters beyond their experimental errors. According to the resonance structures of 4,6-dinitroresorcinol (Scheme 1) the split of the C-C bond lengths should be close to that in 2-nitroresorcinol.^{3,4} This is because there are two possible quinonoid resonance structures of 4,6-dinitroresorcinol stabilized by intramolecular hydrogen bonding and contributing to the overall structure of the molecule. The ΔCC bond length difference in 4,6-dinitroresorcinol refined to a rather larger value, 0.053(5) Å, than in 2-nitroresorcinol³, 0.034(4) Å. Stepwise refinements with this difference being fixed showed a decrease of the *R*-factor when going from 0 to 0.05 Å, and the *R*-factor increased when the difference exceeded 0.05 Å. The changes of other parameters were marginal and within their experimental errors. The ΔCC difference was fixed in subsequent calculations at the more moderate value obtained in the electron diffraction analysis of 2-nitroresorcinol,3 consistent with the ab initio calculations of this molecule.4

The two farthest maxima of the experimental radial distribution have displayed a shift to the lower values as compared with the theoretical radial distribution. This has been observed to be independent of the conditions of refinement. The $N_{16} \cdot \cdot O_{10}$, $O_{13} \cdot \cdot O_{17}$, $O_{14} \cdot \cdot O_{17}$, and $O_7 \cdot \cdot O_{13}$ distances may be supposed to undergo shrinkage and were refined as independent parameters. Treating these distances as independent variables proved sufficient to eliminate the discrepancy while it had no appreciable influence on the other parameters.

The mean amplitudes of vibration were grouped together according to the appearance of the contributions of the corresponding distances on the radial distribution. The differences among them, within the same group belonging to the same maximum, were kept fixed in the refinements. The amplitudes of some nonbonded C··C benzene ring distances were also kept constant at the values obtained in the electron diffraction study of 2-nitroresorcinol.³ We have tested the influence of these assumptions on the other parameters and found that it did not exceed the experimental errors.

The final set of the independent parameters and the results of the electron diffraction least-squares refinements are presented in Table 2. The parameters of this table are effective r_a values

TABLE 2: Results^a of Electron Diffraction Least-Squares Refinement^b of 4,6-Dinitroresorcinol

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type	r _a	la	group ^c	type	r _a	l_{a}	group ^c
Parameters							
(C-C) _{mean}	1.400(1)			∠C₄-C ₁ -0	123.4(2)		
(C-H) _{mean}	1.080(10)	0.078(1)	i	$\angle C_1 - O_7 - H_8$	104.5(10)		
$\Delta CC1/\Delta CC2^{b}$	0.034(5)	. ,		$\angle C_3 - C_4 - N_{12}$	121.0(2)		
ΔCO^d	0.060(2)			$(\angle C - N - O)_{mean}$	118.1(1)		
ΔOH^d	0.084(6)			Te	0.0 ^g		
ΔCN^d	0.060(2)			ϕ^e	14.4(9)		
ΔNO^d	0.168(1)			Ó13 • • • O17	6.983(14)	0.096(13)	ii
$\Delta NO2^d$	$0.016^{8}(11)$			N16 • • • O10	5.575(5)	0.077(5)	iii
ΔCNO^d	$-0.4^{g}(9)$			O7•••O13	6.254(8)	0.091(4)	iv
$\angle C_3 - C_4 - C_5$	121.6(2)			O14 · · ·O17	6.117(9)	0.112	iv
$\angle C_2 - C_3 - C_4$	119.3(2)			- 14 - 17			
	. ,		Dependent Die	stances and Angles			
CC	1 422(3)	0.048	i		6 256(4)	0.091	iv
$C_3 - C_4$	1.422(3) 1.388(2)	0.048	i	$O_7 \cdot \cdot O_{17}$	2 598(6)	0.094	v
$C_2 = C_3$	1.388(2)	0.048	i	$O_7 \cdot \cdot O_{10}$	4 114(4)	0.094	ix
$C_4 = C_3$	1.340(2)	0.044	i		6 990(8)	01071	in the second se
$O_{10} - H_{11}$	0.996(6)	0.079	i	$O_{14} \cdot \cdot \circ O_{17}$	6 136(6)		
C_{10} M_{11}	1.460(2)	0.051	i		4 798(10)	0 134	vii
$(N-\Omega)$	1.400(2) 1.232(1)	0.051	1	$O_{14} = O_{18}$	2 172(1)	0.053	v
Nu-Ou	1.232(1) 1.240(5)	0.043	i	O_{1} O_{18}	2.172(1) 2.554(5)	0.033	v
N ₁₂ O ₁₃	1.240(5) 1.224(5)	0.043	i	07 Hi	5.434(11)	0.140	iii
	1.22+(3)	0.045	1 V		4 581(10)	0.102	vii
Con Co	2.709(7) 2.453(2)	0.055	v	Out tHe	1.712(12)	0.142	i
Crucs	2.433(2) 2.820(4)	0.055	v		1.712(12)	0.103	1
$C_2 \cdots C_5$	2.029(4)	0.0596	V		4.040(9) 6 754(14)	0.173	¥11 11
$C_2 \sim C_6$	2.420(3)	0.055(2)	v		3858(7)	0.102	ir
$C_3 \cdots C_6$	2.703(2) 2.291(2)	0.0596		Out the	3.636(7)	0.145	17
$C_4 \cdots C_6$	2.301(3)	0.055	v		5.507(15)	0.139	**
$C_1 \cdots O_{10}$	5.000(2)	0.037(2)	VI 		5.061(11) 6.442(17)	0.171	111
$C_1 \cdots O_{13}$	4.937(4)	0.083(2)	V11		0.442(17)	0.160	10
$C_1 \cdots C_{14}$	4.930(4)	0.063	vii 	V ₁₈ ···H ₁₅	2.404(3)	0.142	v
$C_1 \cdots O_{17}$	2.790(3)	0.090(3)	viii		2.324(10)	0.137	v
$C_1 \cdots C_{18}$	2,200(4)	0.009	VI		4.040(0)	0.124	VII iv
$C_2 \cdots O_7$	2.330(2)	0.034	v iv		3.933(13)	0.129	1
$C_2 \cdots C_{17}$	4.171(3)	0.098	17		2.044(0) 1.850(12)	0.124	:
$C_{2} + O_{18}$	4.724(4)	0.070	vii		1.639(13)	0.100	1
C3***07	3.092(2)	0.050	vi		2.142(3)	0.107	v iv
C3***O17	3.330(4) 2.701(4)	0.009	VI		4.207(12) 3.425(10)	0.125	1X
C ••• •018	2.701(4)	0.000	VII		3.433(10) 3.120(10)	0.107	viii
$C_{6} = 0_{7}$	2.732(2)	0.052	ir		3.129(10) 3.000(11)	0.113	viii iv
	+.12+(2)	0.00+(2)	17		3.909(11) 3.000(11)	0.114	iv
C6- 013	4.080(3)	0.070	ix		3.765(16)	0.114	IA Vi
	-7.00+(-1)	0.098	IA V		2.703(10)	0.135	VI V
Canolin Canolin	2.310(4) 2.307(3)	0.058	v		2.363(10)	0.140	v
$C_{6} \cdots O_{18}$	2.507(5)	0.038	v iv		3.408(10)	0.105	vi
	7.277(2)	0.071			4.501(15) 2.154(0)	0.105	VII
Crook Nie	2.308(4)	0.057	v	$C_6 - G_{15}$	1203(3)	0.091	v,
$C_2 \sim N_{16}$	5.709(2) 2.435(2)	0.005	VI V	$2C_1 - C_2 - C_3$	118 0(3)		
$C_5 \sim 10_{16}$	2.433(2)	0.057	v	$2C_4 - C_5 - C_6$	117.0(3)		
N	3.704(2) 2.014(4)	0.003	VI VIII	$2C_4 - N_{12} - O_{13}$	117.9(4)		
	2.714(4)	0.065	v111	$2C_4 = N_{12} = O_{14}$	110.3(4)		
NO	5.055(4)	0.111	i	$(\ge 0 - 1 \times - 0)_{mean}$	123.7(1) 18(2)		
IN16**********	3.933(0)	0.111	1V	CN, tht''	1.0(2) 2.1(2)		
IN 16*************	4.9/1(4)	0.129	V11		3.1(2) 146 O(14)		
IN 16***IN 12	4.809(3)	0.114	V11	$\angle U_{10} - m_{11} + U_{13}$	140.0(14)		
$0_7 \cdots 0_{10}$	4.000(4)	0.089	V11	$\angle N_{12} = U_{13} \cdot \cdot \cdot H_{11}$	102.7(7)		
$0_7 \cdot \cdot \cdot 0_{13}$	0.203(4)			K-lactor	2.04%		

^{*a*} r_a bond lengths and bond length differences, all distances, and vibrational amplitudes in ångströms, angles in degrees. ^{*b*} Least-squares standard deviations are parenthesized in units of the last digit. ^{*c*} The amplitudes with the same code were refined in a group with assumed differences between the amplitudes within the group. ^{*d*} Δ CC1 = $r(C_3-C_4) - r(C_2-C_3)$; Δ CC2 = $r(C_3-C_4) - r(C_4-C_5)$; Δ CO = $r(C-C)_{mean} - r(C-O)_{mean}$; Δ OH = $r(C-H)_{mean} - r(O-H)_{mean}$; Δ CN = $r(C-N)_{mean} - r(C-C)_{mean}$; Δ NO = $r(C-C)_{mean} - r(N-O_{13})$; Δ NO2 = $r(N-O_{13}) - r(N-O_{14})$; Δ CNO = $\angle C-N-O_{13} - \angle C-N-O_{14}$. ^{*c*} Angles of torsion are around the C-N bonds, ϕ , and around the C-O bonds, τ . ^{*f*} Assumed from the analysis of 2-nitroresorcinol.³ ^{*h*} Positive when tilt is away from the hydrogen bond. ^{*i*} Angle made by the O-H bond and the hydrogen bond. ^{*j*} Angle made by the hydrogen bond and the N-O bond.

from the least-squares refining routine. Table 3 lists the elements of the correlation matrix exceeding 0.6 in absolute value. For a molecule of this complexity, there are relatively few coefficients in this table. Three of the seven coefficients involve the mean C-C distance, which is well determined and has been proved to be insensitive to various refinement conditions. The Δ NO difference refers to one of the two N-O bond lengths, and the mean N-O bond length, again, is well

determined. The estimated total error of the C–O bond length may be underestimated in view of the relatively strong correlation of Δ CO with Δ NO. However, for consistency, we decided against changing the estimated error limits obtained by a tested procedure¹⁴ that has generally proved to work well. The mean C–H bond length has a large error limit. Finally, the three bond angles with relatively strong correlations have been observed to be well determined in the refinements.

 TABLE 3: Correlation Matrix Elements with Absolute

 Values Greater than 0.6 for 4,6-Dinitroresorcinol

i	j	x _{ij}
$r(C-C)_{mean}$	ΔCO	0.8158
, ,	ΔCΝ	-0.6828
	ΔΝΟ	0.8313
ΔΝΟ	ΔCΟ	0.8392
	∠C ₃ -C ₄ -N	0.6345
∠C−C₄−C	∠C ₄ −C ₃ −O	0.7257
scale 50cm	$r(C-H)_{mean}$	-0.6244

TABLE 4: Bond Lengths $(r_g, Å)$, Bond Angles, and the Angle of Torsion (degrees) of 4,6-Dinitroresorcinol with Estimated Total Errors

C3-C4	1.424 ± 0.005	$\angle C_1 - C_2 - C_3$	120.3 ± 0.4
$(C-C)_{mean}$	1.402 ± 0.003	$\angle C_2 - C_3 - C_4$	119.3 ± 0.3
(C-H) _{mean}	1.086 ± 0.015	$\angle C_3 - C_4 - C_5$	121.6 ± 0.3
C-0	1.341 ± 0.004	$\angle C_4 - C_5 - C_6$	118.0 ± 0.4
O-H	1.002 ± 0.009	∠C ₄ −C ₃ −O	123.4 ± 0.3
C-N	1.461 ± 0.004	∠C ₃ −C ₄ −N	121.0 ± 0.2
(N-O) _{mean}	1.233 ± 0.003	∠0-N-0	123.7 ± 0.2
∠С−О−Н	104.5 ± 1.4	(∠C−N−O) _{mean}	118.1 ± 0.1
$oldsymbol{\phi}^{a}$	14.4 ± 1.3		

^{*a*} Angle of the nitro groups torsion.

Results and Discussion

The main results of the electron diffraction analysis of 4,6dinitroresorcinol with estimated total errors are listed in Table 4. Both systematic errors and least-squares standard deviations were included in the estimation of the total error.¹⁴ The leastsquares standard deviations of Table 2 were obtained in a special calculation in which the assumed parameter differences were also treated as variables to include the influence of the assumptions into experimental errors for a more rigorous error estimation. On the other hand, all electron diffraction studies of the nitrophenol series originate from the same laboratory, and the parameter differences from compound to compound may be more meaningful than the experimental errors might suggest, since some of the systematic errors may cancel in the series.

Resonance effects assist the hydrogen bonding in 4,6dinitroresorcinol similar to those in 2-nitrophenol² and 2-nitroresorcinol.^{3,4} The prominence of the quinonoid forms of 4,6dinitroresorcinol (Scheme 1) demonstrates its structural differences as compared with nitrobenzene and phenol. This simple approach using the resonance model allows a qualitative prediction of the structural variations and is also in agreement with results of ab initio calculations. Table 5 compares the geometrical parameters of 4,6-dinitroresorcinol with those of phenol⁵ and nitrobenzene.⁶ The molecule of 4,6-dinitroresorcinol demonstrates more pronounced changes vs the parent molecules than 2-nitrophenol (cf. Table 5) because it doubles the effects of substitution. The changes in the bond lengths, viz., the shortening of the C–O bond as compared with phenol (0.04 Å), the shortening of the C–N bond as compared with nitrobenzene (0.025 Å), and the lengthening of the C–C bond between the substituents (0.025 Å) as compared with both phenol and nitrobenzene, are fully consistent with the consequences of resonance-assisted hydrogen bonding as discussed previously.³

There seems to be some slight geometrical variation in 4,6dinitroresorcinol as compared with 2-nitrophenol, most pronounced in an approximate 0.01 Å shortening of the C-O bond. This is not well accounted for and not well determined; yet, the ab initio calculations also show this difference.

The nonbonded distances $(N-)O \cdots H(-O)$ and $(N-)O \cdots O$ -(-H) are directly related to the hydrogen bond formation. They are nearly the same, within experimental errors, in 4,6dinitroresorcinol and 2-nitrophenol (Table 5). This suggests similar hydrogen bond strengths in these molecules.

The effective angle of torsion of the nitro groups in 4,6dinitroresorcinol was refined to $14.4 \pm 1.3^{\circ}$. It is larger than the one obtained for 2-nitrophenol, $7.3 \pm 5.7^{\circ}$, the latter value being very uncertain. A planar equilibrium conformation of 2-nitrophenol was predicted by ab initio calculations. If, by analogy with 2-nitrophenol, a planar equilibrium conformation is assumed for 4,6-dinitroresorcinol, then the effective angle of torsion may be attributed to consequences of torsional vibrations in the electron diffraction data. Some decrease of the barrier to torsion may be expected in 4,6-dinitroresorcinol, as compared with 2-nitrophenol, due to the importance of resonance structures stabilized by hydrogen bonding (Scheme 1). According to this model, the nitro group of 4,6-dinitroresorcinol that is not involved in resonance is expected to deviate more readily from the coplanar arrangement than the other nitro group that is involved in resonance. By the lack of the mesomeric interaction between this nitro group and the hydroxy group in the absence of resonance, the steric repulsions between the two substituents may facilitate the out-of-plane motion of the nitro group. The torsion of the other nitro group is greatly restricted. The resonance-averaged structure of 4,6-dinitroresorcinol would

TABLE 5: Comparison of Phenol, Nitrobenzene, 2-Nitrophenol, and 4,6-Dinitroresorcinol Geometrical Parameters (r_g in Angströms and Angles in Degrees) from Electron Diffraction

parameter	phenola	nitrobenzene ^b	2-nitrophenol ^c	4,6-dinitroresorcinol
$C_0 - C_N$	1.399(3)	1.396(3)	1.410(13)	1.424(5)
$N - O(\cdot \cdot \cdot H)$			1.241(9)	1.241(7)
N-O		1.223(3)	1.225(9)	1.225(7)
C-N		1,486(4)	1.467(5)	1.461(4)
C-0	1.381(4)		1.356(9)	1.341(4)
<u>О</u> -Н	0.958(3)		0.967(12)	1.002(9)
∠0-N-0		125.3(2)	123.3(4)	123.7(2)
2C-O-H	106.4(17)		101.8(22)	104.5(14)
$\angle N - C_N - C_O$		118.3(3)	119.9(6)	121.0(2)
$\sqrt{0-C_0-C_N}$	121.2(12)		125.0(8)	123.4(3)
$\angle C - C_N - C$,	123.4(3)	122.4(6)	121.6(3)
$\angle C - C_0 - C$	121.6(2)		118.0(10)	119.3(3)
CO, tilt	+2(1)		+4.0(7)	+3.1(3)
CN, tilt			+1.1(6)	+1.8(2)
$(N-)O \cdot \cdot \cdot H(-O)$			1.71(2)	1.72(2)
$(N-)O \cdot \cdot O(-H)$			2.59(1)	2.60(1)
∠N–O•••H			102.8(14)	102.7(9)
∠0 − H•••O			150(3)	146(2)

^a Reference 5. ^b Reference 6. ^c From a joint analysis incorporating constraints from MP2(FC)/6-31G* ab initio calculations. Note that these parameters are somewhat different from those of ref 2. They originate from a modified refinement as described here in ref 17. ^d Present work.

origin of the data	$\angle C - C_2 - C$, deg	$\angle C - C_3 - C$, deg	$\angle C - C_4 - C$, deg	$\angle C - C_5 - C$, deg	$\Sigma \Delta^2$
X-ray crystallography ^a	119.8	119.3	122.2	117.4	2.17
Electron diffraction ^{b} (phenol + nitrobenzene)	118.6	120.1	122.4	116.6	6.13
Electron diffraction ^c (2-nitrophenol)	119.0	119.9	122.1	117.2	2.94
experimental ^d	120.3(4)	119.3(3)	121.6(3)	118.0(4)	
model implying intersubstituent effects from electron diffraction ^e	120.0	119.5	121.7	117.8	0.18

^{*a*} Additivity scheme using a large number of angular substituent parameters from the solid state.⁷ ^{*b*} Additivity scheme using independent ring distortion parameters from the gas-phase electron diffraction data on phenol⁵ and nitrobenzene.⁶ ^{*c*} Additivity scheme using pairwise interacting ring distortion parameters from the joint gas-phase electron diffraction and ab initio investigation of 2-nitrophenol.¹⁷ ^{*d*} Gas-phase electron diffraction and ab initio investigation of 2-nitrophenol.¹⁷ ^{*d*} Gas-phase electron diffraction angles of 4,6-dinitroresorcinol with estimated total errors in parentheses, present work. Some constraints from ab initio calculations on 2-nitrophenol² were used in the analysis. ^{*e*} Combined model from the electron diffraction results on 2-nitroresorcinol,³ 4,6-dinitroresorcinol, present work, and a modified set of angular parameters of 2-nitrophenol.¹⁷

TABLE 7:	Comparison of Ang	ular Distortion	Parameters of	Nitro and Hyd	droxy Groups	Including or	without Inters	abstituent
Interaction				•	• •	0		

		angul			
Х		Δα	Δeta	Δγ	$\Delta\delta$
$-NO_2$	X-ray crystallography ^b	2.9	-1.9	0.3	0.4
	electron diffraction ^c (nitrobenzene)	3.4	-2.3	0.5	0.2
	model from electron diffraction implying intersubstituent effects ^{d}	3.9	-3.3	2.2	-0.7
-OH	X-ray crystallography ^b	0.2	-0.4	0.6	-0.6
	electron diffraction ^e (phenol)	1.6	-1.2	0.6	-0.3
	model from electron diffraction implying intersubstituent effects ^{d}	1.3	-2.2	2.2	-2.2

^{*a*} See Scheme 2 for the meaning of these parameters. ^{*b*} Additivity scheme using a large number of angular substituent parameters from the solid state.⁷ ^{*c*} Ring distortion parameters from the gas-phase electron diffraction data on nitrobenzene.⁶ ^{*d*} Combined model from the electron diffraction results on 2-nitroresorcinol³ and 4,6-dinitroresorcinol, present work, and a modified set of angular parameters of 2-nitrophenol.¹⁷ ^{*e*} Ring distortion parameters from the gas-phase electron diffraction.

have, therefore, a smaller barrier, on average, to nitro group rotation, and consequently a larger effective angle of torsion, than that of 2-nitrophenol. We would like to stress the model character of this description. Assuming 2-fold rotational potential for the nitro groups, the barrier to rotation can be estimated from the effective angle of torsion,¹⁵ yielding 18 ± 3 kJ/mol, the same as that estimated for nitrobenzene,⁶ 17 ± 4 kJ/mol, for which the assumption of a planar equilibrium structure is consistent with the results of a microwave spectroscopic investigation.¹⁶

The $(C-C)_{mean}$ bond length in 4,6-dinitroresorcinol is well determined $(1.402 \pm 0.003 \text{ Å})$, and it is the same, within experimental error, as that in 2-nitrophenol² $(1.399 \pm 0.003 \text{ Å})$ and in 2-nitroresorcinol³ $(1.404 \pm 0.003 \text{ Å})$.

The alternation of the C-C bond lengths in the benzene ring is pronounced. The C-C bonds between the substituents are considerably longer, while the other C-C bonds are shorter on average. This is consistent with the quinonoid resonance structures of 4,6-dinitroresorcinol.

The angular distortions of the benzene ring in 4,6-dinitroresorcinol are of special interest. Table 6 lists the endocyclic angles of 4,6-dinitroresorcinol along with various estimated sets of angles. One set is obtained by an additivity scheme where the angular distortions originate from a large amount of X-ray crystallographic data on benzene derivatives.⁷ There are two sets based on the electron diffraction results, one of them phenol⁵ and nitrobenzene⁶ and the other 2-nitrophenol (see ref 17), again, using the additivity approach. Yet another set comes from the electron diffraction structures of 2-nitroresorcinol,³ 4,6-dinitroresorcinol itself (present work), and a modified set of angular parameters of 2-nitrophenol.¹⁷ There is marked disagreement between the experimentally determined angles and those deduced from phenol and nitrobenzene. This may (and may not, because of the large experimental errors) indicate the consequence of intersubstituent effects. The agreement obtained from additivity of pairwise interacting substituents from 2-nitrophenol is also poor but considerably better than that for the





gas-phase data on phenol and nitrobenzene. The best agreement is obtained in the comparison with the cumulative data extracted from those three structures with ortho substituents. The agreement here is somewhat overoptimistic since one of the three molecules is 4,6-dinitroresorcinol itself. Table 7 contains the distortion parameters $\Delta \alpha$, $\Delta \beta$, $\Delta \gamma$, and $\Delta \delta$ (see Scheme 2) for the nitro and hydroxy substituents from a large number of crystal structures in which ortho substitution was excluded and from the analogous distortion parameters from the electron diffraction studies of three molecules in which ortho substitution is present. The distortion parameters originating from structures with ortho substitution are markedly larger than those from dataexcluding ortho substitution. It is noted, however, that the consequences of possible intersubstituent effects are not as prominent in the ipso angle as in the rest of the angles.

Conclusions

(1) There is relatively strong, resonance-assisted intramolecular hydrogen bonding in 4,6-dinitroresorcinol, similar to those in 2-nitrophenol and 2-nitroresorcinol.

(2) 4,6-Dinitroresorcinol is of higher symmetry than 2-nitrophenol and doubles the intersubstituent effects. Thus, it is a somewhat better object for an electron diffraction determination of its structure.

(3) There is consistency in the structural changes as a consequence of the hydrogen bond formation in the rest of the

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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.

References and Notes

 $(1)\,$ (a) Institute of General and Analytical Chemistry. (b) Institute of Organic Chemistry.

(2) Borisenko, K. B.; Bock, C. W.; Hargittai, I. J. Phys. Chem. 1994, 98, 1442.

(3) Borisenko, K. B.; Hargittai, I. J. Phys. Chem. 1993, 97, 4080.

(4) Bock, C. W.; Hargittai, I. Struct. Chem. 1994, 5, 307.

(5) Portalone, G.; Schultz, G.; Domenicano, A.; Hargittai, I. Chem. Phys. Lett. 1992, 197, 482.

(6) Domenicano, A.; Schultz, G.; Hargittai, I.; Colapietro, M.; Portalone, G.; George, P.; Bock, C. W. Struct. Chem. **1990**, *1*, 107.

(7) Domenicano, A. In Stereochemical Applications of Gas-Phase Electron Diffraction; Hargittai, I., Hargittai, M., Eds.; VCH: New York, 1988; Part B, Chapter 7.

(8) Gilli, G.; Belucci, F.; Ferretti, V.; Bertolasi, V. J. Am. Chem. Soc. 1989, 111, 1023. Bertolasi, V.; Gilli, P.; Ferretti, V.; Gilli, G. J. Am. Chem. Soc. 1991, 113, 4917.

(9) Typke, P. G. W. Chem. Ber. 1883, 16, 551.

(10) Hargittai, I.; Hernádi, J.; Kolonits, M. Prib. Tekh. Eksp. 1972, 239.
Hargittai, I.; Tremmel, J.; Kolonits, M. Hung. Sci. Instrum. 1980, 50, 31.
(11) Hargittai, I.; Hernádi, J.; Kolonits, M.; Schultz, G. Rev. Sci. Instrum.

(11) Harginal, I., Herhaul, J., Kolonis, M., Schulz, G. Reb. Sci. Instrum.
1971, 42, 546.
(12) (12) (2) Coherent: Bonham P. A : Schöfer, I. In International Tables

(12) (a) Coherent: Bonham, R. A.; Schäfer, L. In *International Tables* for X-ray Crystallography; Kynoch Press: Birmingham, 1974; Vol IV, Chapter 2.5. (b) Incoherent: Tavard, C.; Nicolas, D.; Rouault, M. J. Chim.

Phys. Phys.-Chim. Biol. 1967, 64, 540.

(13) Andersen, B.; Seip, H. M.; Strand, T. G.; Stølevik, R. Acta Chem. Scand. 1969, 23, 3224.

(14) Hargittai, M.; Hargittai, I. J. Chem. Phys. 1973, 59, 2513.

(15) Vilkov, L. V.; Penionzhkevich, N. P.; Brunvoll, J.; Hargittai, I. J. Mol. Struct. 1978, 43, 109.

(16) Høg, J. H. A Study of Nitrobenzene. Thesis, University of Copenhagen, 1971.

(17) Using the benzene ring angles obtained in the structure analyses of 2-nitroresorcinol and 4,6-dinitroresorcinol, we calculated a set of angular distortion parameters for the nitro and hydroxy groups. Solving the system of eight equations (eight independent benzene ring angles in the two molecules), we obtained eight angular distortion parameters ($\Delta \alpha$, $\Delta \beta$, $\Delta \gamma$, and $\Delta \delta$) for the nitro and hydroxy groups. One might have expected to approximate the experimental geometry of 2-nitrophenol using these estimates. However, the agreement was rather poor between the benzene ring angles obtained using the additivity and the experimental values. Even the bond angles from a least-squares refinement based on all three molecules failed to reproduce well the angular parameters of 2-nitrophenol, while the agreement remained good for 2-nitroresorcinol and 4,6-dinitroresorcinol. We have now repeated the analysis of the 2-nitrophenol structure assuming some benzene ring angles at values obtained from the additivity scheme with distortion parameters originating from 2-nitroresorcinol and 4,6dinitroresorcinol. Assuming the $C-C_0-C$ angle to be 118.0°, there is no important change in the other parameters. The R-factor increases to 2.86% against 2.73% reported in the original paper. However, this does not mean an appreciable change in the agreement between the calculated and experimental molecular intensities even at the 99% significance level (cf., Hamilton, W. C. Statistics in Physical Science; The Ronald Press: New York, 1964). The new set of benzene ring angles of 2-nitrophenol according to these calculations is: $C-C_N-C$, $122.4 \pm 0.6^{\circ}$; $C-C_0-C$, $118.0 \pm 1.0^{\circ}$; $C-C-C_N$, $118.6 \pm 0.9^{\circ}$; $C-C-C_0$, $119.5 \pm 1.9^{\circ}$; C-C-C (opposite to $C-C_N-C$), $121.9 \pm 0.9^{\circ}$; C-C-C (opposite to $C-C_0-C$), $119.7 \pm 0.9^{\circ}$. This set of endocyclic angles of 2-nitrophenol, along with those of 2-nitroresorcinol and 4,6-dinitroresorcinol, enabled us to obtain angular distortion parameters by least-squares refinement. The two sets of angular distortion parameters for the nitro and hydroxy substituents are listed in Table 7. They show internal consistency among the three structures and appear to describe well the ring deformation for ortho-substituted derivatives employing additivity.

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