On the Molecular Structure of *o*-Dicyanobenzene as Studied by Electron Diffraction

György Schultz[a], Jon Brunvoll*[b] and Arne Almenningen[c]

[a]Department of Structural Studies, Research Laboratory for Inorganic Chemistry, Hungarian Academy of Sciences, P.O. Box 117, H-1431, Hungary, [b]Division of Physical Chemistry, University of Trondheim, N-7034 Trondheim, Norway and [c]Department of Chemistry, University of Oslo, Blindern, Oslo 3, Norway

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The molecular structure of *o*-dicyanobenzene was studied by gas electron diffraction at a 163 °C nozzle temperature. Overall C_{2v} symmetry of the molecule was assumed in the analysis. The benzene ring is found to be undistorted. The C–C bonds from the CN groups to the ring bisect the adjacent angles of the ring and the C–C≡N groups are linear or nearly linear. The bond lengths (r_a) and bond angles with estimated total errors are: $(C–H)_{mean}$ 1.087 ± 0.005 Å, C≡N 1.161 ± 0.002 Å, $(C\cdots C)_{mean}$ 1.395 ± 0.005 Å, C–C(N) 1.444 ± 0.011 Å, C(H)···C(C-N)···C(CN) 120.2±0.5°, C(N)–C(CN···C(CN) 120.0 ± 1.5°.

The gas electron diffraction method (ED) has been used extensively for determination of ring distortion in monosubstituted, and symmetrically 1,4-disubstituted and 1,3,5-trisubstituted benzene derivatives (see Refs. 1, 2 and references therein). Complete r_s structure of the benzene ring in some important monosubstituted benzene derivatives has been determined by microwave spectroscopy (MW) (see Ref. 3 and references therein). The ring distortion in cyanobenzene and *p*-dicyanobenzene has been determined by MW[4] and ED[5], respectively. Here we present the results of an electron diffraction study of *o*-dicyanobenzene. Recently Diehl and co-workers[6] have determined the r_α structure of this molecule in solvents by NMR spectroscopy.

Experimental

A commercial sample (Aldrich Chemical Co) was used without further purification. The electron diffraction patterns were taken with the Oslo apparatus[7] at the camera distances of 20 and 48 cm. The nozzle temperature was about 163 °C and the electron wavelength was 0.06470 Å. Five plates (Kodak Electron Image) from each camera distance were selected for analysis. The plates were traced using a Joyce Loebl densitometer. The ranges of intensity data used were $2.0 \leq s \leq 18.0$ Å^{-1} with $\Delta s = 0.125$ Å^{-1} and $10.25 \leq s \leq 41.25$ Å^{-1} with $\Delta s = 0.25$ Å^{-1} from the long and short camera distances, respectively. The data reduction procedure was carried out according to the Oslo scheme[8]. The reduced molecular intensities are shown in Fig. 1.

The radial distribution functions are presented in Fig. 2. They were calculated using an artificial damping factor equal to 0.002 Å^2, and theoretical values in the region $0.0 \leq s \leq 2.0$ Å^{-1}.

Structure analysis

Planarity and C_{2v} symmetry were assumed for the molecule. Angular distortion for the benzene ring was allowed in all refinements.

All C···C bond lengths in the ring were assumed equal. All C–H bond lengths were assumed equal, and directed along bisectors of the adjacent ring angles.

The geometry of the CCN moieties was charac-

*To whom correspondence should be addressed.

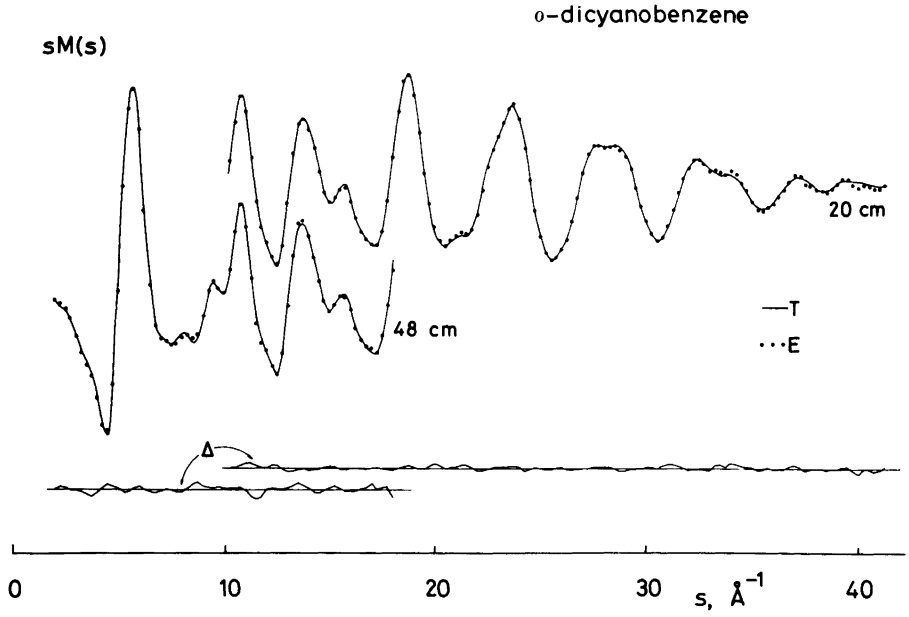

Fig. 1. Experimental (E) and theoretical (T) molecular intensities and their differences (Δ) for refinement D.

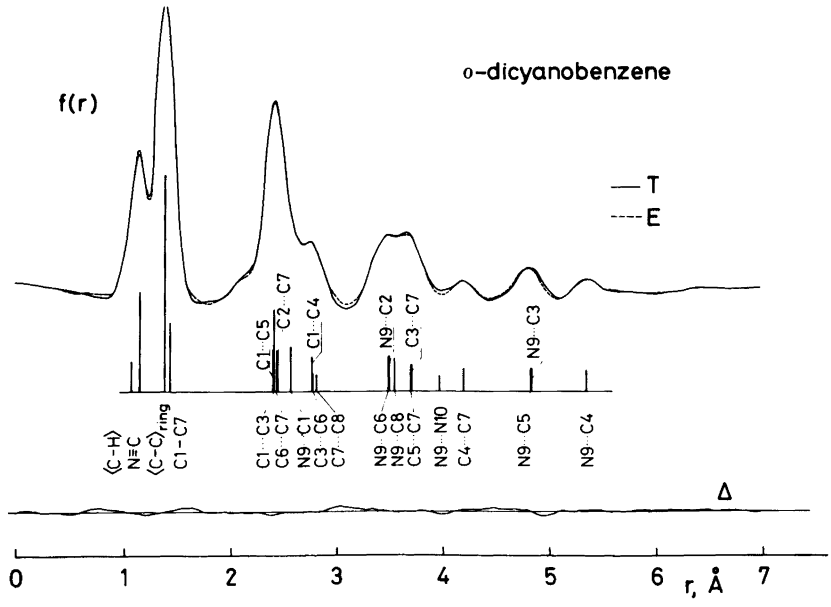

Fig. 2. Experimental (E) and theoretical (T) radial distribution curves and their differences (Δ) for refinement D. The positions of the most important distances are marked with vertical bars, their height is proportional to the relative weight of the distances.

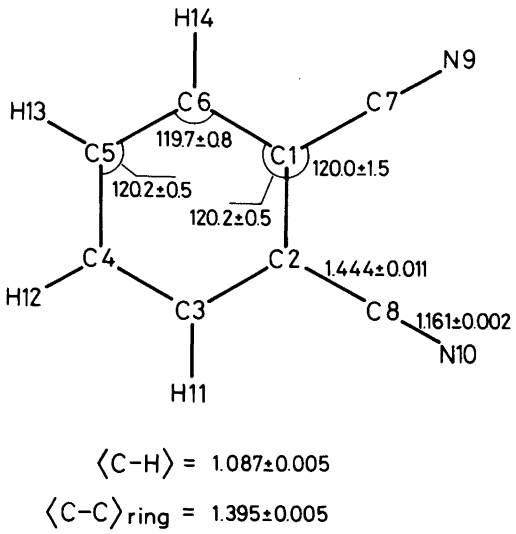

Fig. 3. Molecular geometry of *o*-dicyanobenzene as determined by electron diffraction. Bond distances (r_g) are given in Å, angles in degrees. The estimated total errors are also given.

terized by C–C(N) and C≡N bond lengths and by the amount of deviation by C–C≡N bond angles from linearity (Φ) under the constraint of C_{2v} molecular symmetry. A positive Φ indicates that the CN groups are being tilted away from each other. An alternative approach was fixing Φ at o° and introducing shrinkage parameters for the N9...C1 (N10...C2) and N9...C4 (N10...C5) distances. The C2C1C7 = C1C2C8 angles characterizing the orientation of the CN substituents were also refined. The numbering of atoms in the molecule is shown in Fig. 3.

The least squares refinement was applied to molecular intensities[8]. The initial values of the mean square amplitudes were taken from spectroscopic calculations based on experimental vibrational frequencies[9]. They were refined in blocks coupling the amplitudes of near lying distances.

The results of the least square refinements for four different models (A–D) are presented in Table 1. In model A Φ = o° and shrinkages are ignored; while angle Φ was refined in models B and C. Depending on initial values, two minima were obtained. Model D is similar to model A except that shrinkages were allowed for the N9...C1 (N10...C2) and N9...C4 (N10...C5) distances.

The results for model D are presented in more detail in Table 2, which also contains calculated parallel (l^{sp}) and perpendicular (K) mean square amplitudes.

Models B and D proved to be superior to A and C in fitting the experimental data, as is seen by the R-factors. As regards the choice between B and D, model D was preferred as earlier ED studies on *p*-dicyanobenzene[5] indicated consider-

Table 1. Geometrical parameters[a] and R-factors as obtained for models A–D for the *o*-dicyanobenzene molecule.

Parameters	A	B	C	D
$(C\cdots C)_{mean}$	1.3978(5)	1.3955(3)	1.3970(4)	1.3938(6)
C1–C7	1.425(2)	1.435(1)	1.428(2)	1.442(3)
N≡C	1.1600(5)	1.1599(4)	1.1597(5)	1.1597(5)
$(C-H)_{mean}$	1.078(3)	1.078(3)	1.082(4)	1.082(4)
∡C2···C1···C6	120.0(2)	120.2(2)	119.5(2)	120.2(2)
∡C1···C6···C5	120.0(3)	119.6(3)	120.9(4)	119.7(4)
∡C6···C5···C4	120.0(2)	120.2(2)	119.6(2)	120.2(2)
∡C2···C1···C7	119.5(2)	122.2(2)	119.1(3)	120.0(2)
∡C1–C7≡N9	0.0[b]	−7.2(6)	7.0(9)	0.0[b]
δ (N9...C1)[c]	0.0[b]	0.0[b]	0.0[b]	0.019(4)
δ(N9...C4)[c]	0.0[b]	0.0[b]	0.0[b]	0.020(9)
R (%)	5.56	5.35	5.59	5,32

[a]Bond distances (r_a) and shrinkage parameters are given in Å, bond angles in degrees. Least squares standard deviations are given in parentheses as units in the last digit. [b]Fixed value. [c]Shrinkages.

Table 2. The molecular parameters for *o*-dicyanobenzene as obtained for model D[a].
(a) Distances, mean amplitudes of vibrations (Å).

Atomic pair	Multiplicity	r_a	l^{ed}	key to the coupling scheme	l^{sp}	K
$(C–H)_{mean}$	4	1.082(3)	0.0740(7)	i	0.0766	0.02080
N9≡C7[b]	2	1.1597(5)	0.0318	i	0.0348	0.02268
$(C\cdots C)_{mean}$[b]	6	1.3938(5)	0.0453(8)	ii	0.0469	0.00568
C1–C7	2	1.442(3)	0.0478	ii	0.0495	0.00757
C1...C5	2	2.410(6)	0.0591(8)	iii	0.0564	0.00524
C1...C3	2	2.416(3)	0.0567	iii	0.0539	0.00451
C6...C4	2	2.416(3)	0.0620	iii	0.0593	0.00784
C6...C7	2	2.454(2)	0.0682	iii	0.0655	0.00836
C2...C7	2	2.456(3)	0.0636	iii	0.0609	0.00558
N9...C1	2	2.583(2)	0.051(2)	iv	0.0534	0.00760
C1...C4	2	2.784(5)	0.071(2)	v	0.0609	0.00455
C3...C6	1	2.794(9)	0.072	v	0.0619	0.00598
C7...C8	1	2.836(7)	0.092	v	0.0818	0.00691
N9...C6	2	3.511(3)	0.114(3)	vi	0.0685	0.00631
N9...C2	2	3.512(3)	0.113	vi	0.0669	0.00382
N9...C8	2	3.560(9)	0.135	vi	0.0891	0.00485
C5...C7	2	3.730(4)	0.069(2)	vii	0.0665	0.00480
C3...C7	2	3.735(3)	0.065	vii	0.0623	0.00427
N9...N10	1	3.99(1)	0.100(4)	viii	0.0978	0.00534
C4...C7	2	4.227(4)	0.070	viii	0.0671	0.00262
N9...C5	2	4.842(4)	0.095(4)	ix	0.0691	0.00290
N9...C3	2	4.846(3)	0.093	ix	0.0672	0.00183
N9...C4	2	5.366(8)	0.086(6)	x	0.0684	0.00146
C4...H13	2	2.149(3)	0.092(4)	xi	0.1001	0.01890
C6...H13	2	2.149(3)	0.093	xi	0.1008	0.01812
C1...H14	2	2.151(3)	0.092	xi	0.0996	0.01519
C5...H14	2	2.151(3)	0.092	xi	0.0997	0.01586
C7...H14	2	2.674(4)	0.129	iv	0.1310	0.01746
C1...H13	2	3.391(6)	0.087(7)	xii	0.0960	0.01347
C3...H13	2	3.395(3)	0.087	xii	0.0961	0.01638
C2...H14	2	3.397(4)	0.085	xii	0.0936	0.01114
C4...H14	2	3.397(4)	0.086	xii	0.0953	0.01450
N9...H14	2	3.492(4)	0.186	vi	0.1403	0.01367
C2...H13	2	3.866(6)	0.098	vii	0.095	0.01175
C3...H14	2	3.876(9)	0.098	vii	0.0950	0.01170
C7...H13	2	4.600(4)	0.11(2)	xiii	0.1114	0.01052
C8...H14	2	4.605(5)	0.10	xiii	0.1056	0.00899
C8...H13	2	5.308(5)	0.112	x	0.0991	0.00674
N9...H13	2	5.653(4)	0.12(3)	xiv	0.1157	0.00730
N10...H14	2	5.657(5)	0.12	xiv	0.1151	0.00496
N10...H13	2	6.468(5)	0.11(5)	xv	0.0999	0.00505
H12...H13	1	2.473(5)	0.159		0.1594	0.02558
H13...H14	2	2.477(4)	0.159		0.1599	0.02288
H11...H13	2	4.289(6)	0.130		0.1300	0.02060
H11...H14	1	4.957(11)	0.119		0.1194	0.01516

Table 2. (continued)
(b) Bond angles (°), differences between bond distances and shrinkages (Å).

Parameter	Value
∡C6···C1···C2[b]	120.1(2)
∡C1···C6···C5	119.7(4)
∡C6···C5···C4	120.1(2)
∡C2···C1···C7[b]	120.0(2)
∡C1–C7≡N9	0.0[c]
δ(N9...C1)[b,d]	0.019
δ(N9...C4)[b,d]	0.020(9)
Δ_1[b,e]	0.078(3)
Δ_2[b,f]	0.048(3)

[a]Least-squares standard deviations are given in parentheses as units in the last digit. [b]Independent parameters. [c]Assumed value. [d]The shrinkage is defined here as the decrease in a non-bonded distance when refined as independent parameter, as compared with the value calculated by employing geometrical constrains. [e]$\Delta_1 = r(N{\equiv}C) - r(C{-}H)$. [f]$\Delta_2 = r(C1{-}C7) - r(C\cdots C)_{mean}$.

Table 3. Correlation matrix elements (ϱ) having absolute value greater than 0.5 as obtained from refinement D.

i	j	ϱ_{ij} ($i \neq j$)
$r(C\cdots C)_{mean}$	δ(N9...C1)	−0.763
	Δ_2	−0.914
	$l(C\cdots C)$	0.709
	l(C1...C5)	0.544
∡C6···C1···C2	δ(N9...C1)	0.641
	Δ_2	0.561
δ(N9...C1)	Δ_2	0.831
	$l(C\cdots C)$	−0.703
	l(C1...C5)	−0.573
$l(C\cdots C)$	Δ_2	−0.795
l(C1...C5)	Δ_2	−0.600
	$l(C\cdots C)$	0.746
l(C8...H14)	l(N9...C5)	0.555
Sc1[a]	$l(V\cdots C)$	0.525
SC1[a]	l(C–H)	0.615

[a]Scale factor for short camera distance data.

able shrinkages related to the internal motion of the CN substituents. This choice was also supported by the good agreement between the electron diffraction and spectroscopic shrinkage parameters (see below).

The bond lengths (r_g) and bond angles obtained for model D are presented in Fig. 3. The total errors were estimated according to

$$\sigma_t = [(0.002r)^2 + 2\sigma^2 + (\Delta/2)^2]^{\frac{1}{2}}$$

for distances and

$$\sigma_t = [2\sigma^2 + (\Delta/2)^2]^{\frac{1}{2}}$$

for angles[10], where σ is the standard deviation as obtained from least squares refinement and Δ is the maximum difference in the four sets of results A–D. The elements of the correlation matrix exceeding 0.5 for refinement D are given in Table 3.

Refinements A–D have been repeated allowing for some difference in the bond lengths of the benzene ring: the C3···C4, C4···C5, and C5···C6 bond lengths were put equal to 1.397 Å, that is to the C···C bond length in the ben-

Table 4. The bond lengths (r_a) of *o*-dicyanobenzene as determined by ED and NMR[a].

	ED	NMR
C6–H14		1.067±0.010
C5–H13		1.080±0.002
$(C{-}H)_{mean}$	1.066±0.005	1.073
N≡C	1.138±0.002	1.110±0.034
C1···C2		1.407±0.006
C2···C3		1.407±0.022
C3···C4		1.402±0.008
C4···C5		1.391±0.007
$(C\cdots C)_{mean}$	1.389±0.005	1.403
C1–C7	1.436±0.011	1.438±0.023

[a]Bond lengths in Å.

zene molecule, and the remaining bond lengths were refined. These attempts, however, did not decrease the R-factor, or, in some cases, did so while refining some of the amplitudes to unacceptable values.

Discussion

The r_α bond distances of the *o*–dicyanobenzene molecule as obtained from the present study are compared in Table 4 with those obtained by NMR spectroscopy from analysis of proton spectra including ^{13}C- and ^{15}N-satellites in isotropic and oriented solvents[6]. The r_α bond lengths in the present study were calculated according to the equation[11]

$$r_\alpha = r_a + \frac{l^2}{r} - K,$$

where K is the perpendicular amplitude correction given in Table 2. The NMR internuclear distances are based on r(H11...H14) = 4.96 Å, the r_α value for this distance obtained in the present study is 4.945 Å. Due to this difference slightly higher values are expected for the NMR distances as compared with the ED r_α distances. Taking into account the uncertainties of the NMR data, and that the errors of the electron diffraction r_α bond lengths are no less than those for r_g bond lengths (Fig. 3), the agreement between the two data sets is satisfactory. Both studies indicate that the benzene ring is undistorted within experimental error, and the C–C≡N group is linear or nearly linear. The NMR results show that the substituents are tilted away from each other (Φ is about 2°).

The shrinkage parameters were calculated from spectroscopic data according to the following expressions[12]:

$$\delta(\text{N9...C1}) = \frac{l_{19}^2}{r_{19}} - \frac{l_{17}^2}{r_{17}} - \frac{l_{79}^2}{r_{79}} - K_{19} + K_{17} + K_{79}$$

and

$$\delta(\text{N9...C1}) = \frac{l_{49}^2}{r_{49}} - \frac{l_{47}^2}{r_{47}} - \frac{l_{79}^2}{r_{79}} - K_{49} + K_{47} + K_{79}$$

The obtained values 0.0210 Å and 0.0226 Å are in good agreement with the electron diffraction results given in Table 2. In accordance with an earlier study of *p*-dicyanobenzene[5], the shrinkage of the N7...C4 distance was ignored. The bond lengths obtained for the *o*-dicyanobenzene molecule are identical with corresponding bond lengths of *p*-dicyanobenzene molecule. In cyanobenzene and in *p*-dicyanobenzene, due to the strongly σ-electron withdrawing –CN functional group, the benzene ring departs significantly from a regular hexagonal structure. The angular distortion is most pronounced at the ipso atom. In cyanobenzene the corresponding angle is 121.82 ± 0.05, and in *p*-dicyanobenzene it is 122.1 ± 0.2°. The ED and NMR results indicate that the substituent effects from the two cyano groups cancel each other in *o*-dicyanobenzene.

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