

The Crystal and Molecular Structure of 2,2'-Di(1,4-naphthoquinone)

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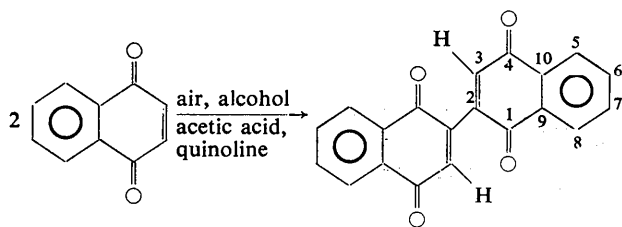
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(Received 19 March 1968)

2,2'-Di(1,4-naphthoquinone), (C₁₀H₅O₂)₂, crystallizes in the monoclinic space group *C2/c* with unit-cell parameters $a=26.274$, $b=3.774$, $c=16.145$ Å and $\beta=118.51^\circ$. There are four molecules, eight C₁₀H₅O₂ units, per unit cell. Intensity data were collected on film and by diffractometer, using Cu K α radiation; the structure was solved by interpretation of the $h0l$ and three-dimensional Patterson functions. The center of each molecule is coincident with a crystallographic rotation diad rather than the originally postulated center of symmetry. Refinement was by full-matrix least squares; carbon and oxygen positional and anisotropic temperature factors, and hydrogen positional and isotropic temperature factors, were varied simultaneously to give a final *R* index of 0.049. An O(1)···H(3') separation of 2.56 Å is achieved by a 47.3° twist of the two naphthoquinone halves about the C(2)–C(2') bond. The quinone ring deviates slightly from planarity with the benzene ring, assuming a shallow chair shape. Bond lengths have been corrected for the effects of thermal oscillation. The mean of the six C–C bonds in the benzene nucleus is 1.392 Å. Standard deviations in the bond lengths are C–O = 0.0025, C–C = 0.0027 and C–H = 0.03 Å.

Introduction

The oxidative coupling of 1,4-naphthoquinone to 2,2'-di(1,4-naphthoquinone) (DNQ) was described 30 years ago by Pummerer and his co-workers (Rosenhauer, Braun & Pummerer, 1937; Pummerer, Pfaff, Riegelbauer & Rosenhauer, 1939). Hand & Cohen (1967) have recently clarified the structure of the hydra-



zone of DNQ. In a preliminary X-ray investigation of DNQ, Sundaralingam (1961) reported the monoclinic space group *P2₁/a* and a crystal density measurement which indicated the presence of only two molecules per unit cell, half the number of symmetry equivalent positions. Barring disorder, these observations restrict the molecule to the *s-trans* configuration shown above, with the two halves related by a center of symmetry. The two naphthoquinone moieties must therefore be parallel to each other, giving two structural possibilities: (a) the two halves are not coplanar but offset, causing deformation of the *sp*² carbons, C(2) and C(2'), or (b) the two halves are coplanar, producing severe non-

bonded interactions between O(1)···H(3') and O(1')···H(3). The extent of molecular distortion should be appreciable in either case and an investigation of this phenomenon provided the basic stimulus for our work.

Additional interest in DNQ was generated by the suggestion of Prout & Wallwork (1966) that in certain crystal structures a specific interaction between a carbonyl group and an aromatic ring may occur. This type of interaction, which was found in 1,4-naphthoquinone (Gaultier & Hauw, 1965*a*), might possibly be observed in the present study. The 1,4-naphthoquinone moiety is also a component of vitamin K (antihemorrhagic factor), and although there have been a number of investigations of 1,4-naphthoquinone derivatives by the French group (Gaultier & Hauw, 1966), there is little structural information for the system in the absence of powerful electron donating and withdrawing substituents. It is interesting that 2-methyl-1,4-naphthoquinone is a more potent antihemorrhagic factor, on a weight basis, than vitamin K₁. In the present work, a considerable effort was placed on obtaining precise dimensions for the naphthoquinone system.

Experimental

DNQ crystallizes in the monoclinic system as yellow needles elongated along the *b* axis. Systematic absences from Weissenberg and precession photographs (Cu and Mo radiation), $0k0$ absent for *k* odd, $h0l$ absent for *l* odd and hkl absent for $h+k$ odd, were consistent with

the space groups $C2/c$ ($Z=8$) or Cc ($Z=4$). Sundaralingam's (1961) cell constants were used in the initial part of our study. The length of the a axis has been doubled to account for the centered lattice:

$$a=26.44, b=3.80, c=16.29 \text{ \AA}; \beta=118.7^\circ.$$

The measured density, 1.48 g.cm^{-3} , was consistent with four molecules per unit cell. Weissenberg photographs were collected with $\text{Cu } K\alpha$ radiation for a crystal rotated about the b axis ($h0l$ to $h3l$). The spots were integrated in a direction perpendicular to the crystal rotation axis and subsequently scanned with a microdensitometer in a direction parallel to the crystal rotation axis. The areas under the densitometer traces were measured with a planimeter (657 observed reflections). The irregular crystal shapes did not facilitate mounting about another axis and exposure times were subsequently used to approximate the level-to-level scaling factors.

The short b axis would be expected to limit the angle of tilt of the naphthoquinone rings with respect to the (010) plane. A maximum tilt of 25.7° was calculated using 3.4 \AA as the thickness of the molecule. The (010) projection was readily solved, in the centric, two-dimensional plane group $p2$, by interpretation of the Patterson function; subsequent least-squares refinement, based on individual isotropic temperature factors and 114 observed data, gave an R index of 0.10. The projection bond lengths were unreliable (e.g. $\text{C}(5)\text{--}\text{C}(10)=1.44 \text{ \AA}$, and $\text{C}(7)\text{--}\text{C}(8)=1.48 \text{ \AA}$ in the benzene ring) and could not be used to verify the molecular tilt. Refinement in the acentric plane group $p1$ was not attempted because of the increase in the number of parameters.

Although the structure was solved in a centric projection, the acentric space group Cc could not be excluded. Normalized structure factors, E 's, were calculated and the values of $|E|$ and $|E^2-1|$ compared with the theoretical distributions for centric and acentric space groups (Karle & Britts, 1966). The results were ambiguous and suggested a pseudocentric space group. It was felt that the absence of good level-to-level scale factors could have caused a failure of the above test. Consequently, complete three-dimensional data were recollected on an automated Picker four-angle diffractometer using $\text{Cu } K\alpha$ radiation. A least-squares refinement of the cell constants employing carefully measured values of 2θ for twelve reflections gave:

$$a=26.274 \pm 0.004, b=3.7735 \pm 0.0003,$$

$$c=16.145 \pm 0.003 \text{ \AA} \text{ and } \beta=118.51 \pm 0.01^\circ$$

$$(\lambda_{\text{Cu } K\alpha}=1.5418 \text{ \AA}).$$

Intensities were measured by the 2θ scan technique with scan ranges calculated from the equation of Alexander & Smith (1964). Stationary background measurements were made for ten seconds at the start and finish of each scan. Three standard reflections were measured after each 80 reflections to monitor crystal decomposi-

tion, X-ray beam intensity variations, etc. An overall decrease of ca. 1% was observed in the standards from the start to the end of the data collection.

Appropriate corrections were made to bring each set of background measurements and 2θ intensity scan to the same time scale. If the peak count, calculated by subtraction of the corrected background counts (I_b) from the scan counts (I_s), was less than 1σ of the measurement ($\sigma=(I_s+I_b)^{1/2}$), the reflection was considered unobservable and assigned the minimum intensity of 1σ . Of the 1177 reflections measured out to $2\theta \simeq 130^\circ$, 1114 (95%) were observed and 63 were unobserved. The 130° limit in 2θ was necessitated by collision of the full-circle goniostat with the primary X-ray beam collimator. The intensities were converted to structure factors in the normal way. Absorption corrections were not applied because of the small linear absorption coefficient, 8.7 cm^{-1} , and modest crystal dimensions, $0.05 \times 0.1 \times 0.2 \text{ mm}$.

The distribution of E 's, calculated from the diffractometer data, clearly indicated the centric space group, $C2/c$. The asymmetric unit therefore contains only half of the DNQ molecule and the two halves can now be related either by an inversion center or by a twofold rotation axis. In the latter case the two naphthoquinone planes can minimize the $\text{O} \cdots \text{H}$ nonbonded interactions by rotation about the $\text{C}(2)\text{--}\text{C}(2')$ bond.

Least-squares refinement of the two-dimensional structure using the 198 $h0l$ diffractometer data gave an R of 0.11. Bonds which were parallel to the plane of projection should appear normal in length whereas all others should be somewhat shorter than normal. The distances for $\text{C}(2)\text{--}\text{C}(2')=1.493$, $\text{C}(1)\text{--}\text{C}(9)=1.486$ and $\text{C}(3)\text{--}\text{C}(4)=1.482 \text{ \AA}$ were normal for $\text{C}(sp^2)\text{--}\text{C}(sp^2)$ single bonds, while $\text{C}(5)\text{--}\text{C}(10)=1.384$ and $\text{C}(7)\text{--}\text{C}(8)=1.417 \text{ \AA}$ were reasonable for aromatic $\text{C}\text{--}\text{C}$ bonds. The $\text{C}(6) \cdots \text{C}(9)$ distance of 2.78 \AA was in excellent agreement with the length of 2.79 \AA , calculated for a regular hexagon of side length 1.395 \AA . The average of the $\text{C}(5) \cdots \text{C}(7)$ and $\text{C}(8) \cdots \text{C}(10)$ distances, 2.26 \AA , compared to the $\text{C}(1) \cdots \text{C}(3)$ distance of 2.42 \AA for the perfect hexagon, was used to calculate a tilt of 21° from the (010) plane.

The two-dimensional coordinates, x and z , were based on the assumption that the $\text{C}(2)\text{--}\text{C}(2')$ bond center lies at 0, 0. If the molecule, however, were occupying the twofold axis, the bond center would be at $0, \frac{1}{2}$. Two sets of coordinates were developed (x, z and $x, \frac{1}{2}+z$) corresponding to the two possible arrangements, and the origin-removed sharpened Patterson function, calculated using $|E^2-1|$ for the Fourier coefficients, was searched for vector density at $2x, v, 2z$ and $2x, v, \frac{1}{2}+2z$. Reasonable values of v for all atoms were found in the latter case only, and the anticipated molecular tilt of $20\text{--}25^\circ$ was verified. The coordinates were further substantiated by a large peak on the Harker line at $2y=0.14$. A structure factor calculation at this point, using the y 's from the Patterson, and x 's, $\frac{1}{2}+z$'s and B 's from the two-dimensional work, and data out to

THE CRYSTAL STRUCTURE OF 2,2'-DI(1,4-NAPHTHOQUINONE)

Table 1. Observed and calculated structure factors

Table of observed and calculated structure factors for 2,2'-di(1,4-naphthoquinone). The table is organized into numerous blocks, each corresponding to a different reflection order (k, l, h). Each block contains columns for observed structure factors (hkl) and calculated structure factors (hk0, h0l, hkl). The data includes observed values, calculated values, and E-values for unobserved reflections. The blocks are labeled with Miller indices such as h, 10F0, and 10F1.

The data are listed in blocks of constant k and l. The three columns within each block are h, 10F0 and 10F1. Unobserved reflections are marked with an asterisk and all reflections not included in the least-squares calculations are marked with an E.

$\sin \theta/\lambda=0.45$, gave an R of 0.16. Two cycles of least squares on y 's and B 's gave $R=0.13$.

Refinement of C, O and H parameters

All least-squares refinement cycles were calculated with the full matrix of the normal equations. The majority of the calculations in this work were performed by the *X-ray 63* programs on an IBM 7094 computer. Atomic form factors used were the following: carbon and oxygen, Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955); hydrogen, Stewart, Davidson & Simpson (1965).

Three cycles of least squares on the full data with unit weights and individual anisotropic temperature factors for the carbon and oxygen atoms gave an R of 0.087. A difference map at this stage clearly revealed the five hydrogen positions. When the hydrogens were included, the index dropped to 0.067. It was possible to refine all of the atoms simultaneously, the hydrogens with isotropic temperature factors and the carbons and oxygens with anisotropic temperature factors. In all, there were 129 parameters, including one scale factor. Several additional cycles of least squares with Hughes (1941) weights, $4F_{\min}=30$, gave a final R of

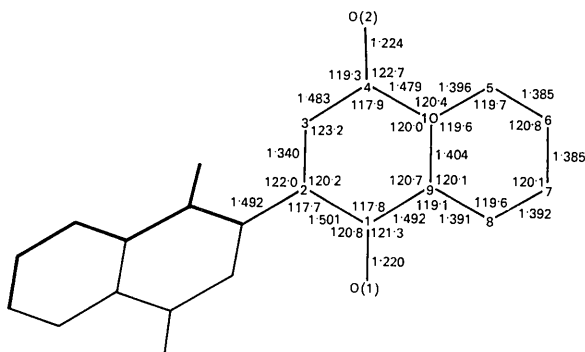


Fig. 1. Bond lengths (Å) and bond angles (°) corrected for the effects of thermal motion.

0.049. The unobserved reflections were included in the refinement with the following weights: $w=0$ if $F_o \leq F_c$ and $w=1.0$ if $F_o > F_c$. At the end of the last cycle, none of the 63 unobserved reflections had $F_c > F_o$. Nine intense reflections with $F_o > 90$ showed the effects of secondary extinction ($F_o < F_c$) and were omitted in the final refinement cycles. The average change in the 129 parameters during the last cycle of least squares was 0.21σ and the maximum was 0.64σ . The measured and calculated structure factors are shown in Table 1.

Discussion

The atomic positional and thermal parameters, with their estimated standard deviations, are given in Table 2. Bond lengths have been corrected for thermal oscil-

Table 3. Bond lengths with estimated standard deviations

	Bond length	
	Uncorrected	Corrected
C(1)–C(2)	1.496 ± 0.003 Å	1.501 Å
C(1)–C(9)	1.488 ± 0.002	1.492
C(1)–O(1)	1.215 ± 0.002	1.220
C(2)–C(3)	1.335 ± 0.003	1.340
C(2)–C(2')	1.488 ± 0.002	1.492
C(3)–C(4)	1.479 ± 0.002	1.483
C(4)–C(10)	1.475 ± 0.003	1.479
C(4)–O(2)	1.219 ± 0.003	1.224
C(5)–C(10)	1.392 ± 0.002	1.396
C(5)–C(6)	1.379 ± 0.003	1.384
C(6)–C(7)	1.379 ± 0.004	1.385
C(7)–C(8)	1.388 ± 0.002	1.392
C(8)–C(9)	1.386 ± 0.003	1.391
C(9)–C(10)	1.398 ± 0.003	1.404
C(3)–H(3)	1.00 ± 0.03	1.07
C(5)–H(5)	0.96 ± 0.03	1.04
C(6)–H(6)	0.99 ± 0.02	1.05
C(7)–H(7)	1.00 ± 0.03	1.05
C(8)–H(8)	0.94 ± 0.03	1.00

C–C and C–O bond lengths were corrected for the librational motion about the molecular center of mass (Busing & Levy, 1964). C–H bond lengths were corrected for the 'riding motion' of one atom upon another (Busing & Levy, 1964).

Table 2. Final positional and thermal parameters, with estimated standard deviations

All B values are in \AA^2 with the B_{ij} in the form: $\exp(-0.25[h^2 B_{11} a^{*2} + \dots + 2kl B_{23} b^* c^*])$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O(1)	0.99423 (6)	1.33284 (50)	0.38598 (10)	2.76 (6)	7.30 (10)	3.50 (6)	1.46 (6)	1.45 (5)	-0.53 (7)
O(2)	1.17463 (6)	0.81350 (53)	0.35984 (10)	2.75 (6)	7.98 (11)	3.94 (7)	1.63 (7)	1.60 (5)	-0.51 (7)
C(1)	1.03544 (8)	1.20330 (56)	0.38235 (13)	2.51 (7)	3.72 (9)	3.04 (8)	0.41 (7)	1.44 (6)	0.22 (7)
C(2)	1.02939 (7)	1.05928 (55)	0.29173 (12)	2.26 (7)	3.60 (9)	2.74 (8)	0.02 (7)	1.16 (6)	0.06 (7)
C(3)	1.07593 (8)	0.94425 (61)	0.28686 (14)	2.69 (8)	4.24 (10)	3.11 (8)	0.02 (7)	1.43 (7)	-0.32 (8)
C(4)	1.13461 (8)	0.93484 (60)	0.36906 (13)	2.50 (7)	4.16 (10)	3.29 (8)	0.37 (7)	1.39 (7)	0.08 (8)
C(5)	1.19629 (8)	1.07350 (62)	0.53904 (14)	2.58 (8)	4.33 (11)	3.44 (9)	0.40 (8)	1.19 (7)	0.32 (8)
C(6)	1.20227 (9)	1.19637 (66)	0.62369 (14)	3.05 (9)	4.99 (12)	3.02 (9)	-0.09 (8)	0.69 (7)	0.15 (8)
C(7)	1.15480 (9)	1.31250 (67)	0.63098 (14)	3.83 (9)	4.90 (12)	2.88 (9)	-0.30 (9)	1.36 (7)	-0.30 (8)
C(8)	1.10032 (9)	1.31380 (62)	0.55226 (14)	3.20 (9)	4.30 (10)	3.21 (8)	0.31 (8)	1.71 (7)	0.0 (8)
C(9)	1.09384 (7)	1.19349 (53)	0.46664 (12)	2.49 (7)	3.25 (9)	2.70 (9)	0.13 (7)	1.15 (6)	0.24 (7)
C(10)	1.14184 (7)	1.06943 (54)	0.45980 (12)	2.41 (7)	3.37 (9)	3.00 (8)	0.19 (7)	1.24 (6)	0.32 (7)
H(1)	1.0729 (9)	0.8572 (62)	0.2262 (15)	4.37 (49)					
H(2)	1.2294 (10)	0.9881 (69)	0.5344 (15)	4.67 (52)					
H(3)	1.2414 (10)	1.1971 (64)	0.6792 (16)	4.67 (51)					
H(4)	1.1600 (9)	1.4111 (62)	0.6919 (15)	4.17 (48)					
H(5)	1.0683 (9)	1.3999 (61)	0.5572 (14)	4.11 (48)					

lation effects (Cruickshank, 1956; Busing & Levy, 1964) and the uncorrected and corrected values are given in Table 3; the corrected lengths are also shown in Fig. 1. Table 4 contains bond angles.

Table 4. Bond angles with estimated standard deviations

	Angle
O(1)—C(1)—C(2)	120.81 ± 0.14°
O(1)—C(1)—C(9)	121.31 ± 0.19
C(2)—C(1)—C(9)	117.85 ± 0.19
C(1)—C(2)—C(3)	120.19 ± 0.14
C(1)—C(2)—C(2')	117.74 ± 0.18
C(3)—C(2)—C(2')	122.05 ± 0.19
C(2)—C(3)—C(4)	123.16 ± 0.21
C(3)—C(4)—O(2)	119.34 ± 0.20
C(3)—C(4)—C(10)	117.91 ± 0.20
O(2)—C(4)—C(10)	122.74 ± 0.14
C(6)—C(5)—C(10)	119.71 ± 0.21
C(5)—C(6)—C(7)	120.76 ± 0.16
C(6)—C(7)—C(8)	120.15 ± 0.22
C(7)—C(8)—C(9)	119.60 ± 0.23
C(1)—C(9)—C(8)	119.09 ± 0.19
C(1)—C(9)—C(10)	120.75 ± 0.18
C(8)—C(9)—C(10)	120.15 ± 0.15
C(4)—C(10)—C(5)	120.37 ± 0.19
C(4)—C(10)—C(9)	120.03 ± 0.14
C(5)—C(10)—C(9)	119.60 ± 0.19
C(2)—C(3)—H(3)	121.2 ± 1.2
C(4)—C(3)—H(3)	115.6 ± 1.2
C(6)—C(5)—H(5)	120.6 ± 1.2
C(10)—C(5)—H(5)	119.7 ± 1.2
C(5)—C(6)—H(6)	118.3 ± 1.7
C(7)—C(6)—H(6)	120.9 ± 1.7
C(6)—C(7)—H(7)	120.0 ± 1.2
C(8)—C(7)—H(7)	119.8 ± 1.2
C(7)—C(8)—H(8)	119.8 ± 1.2
C(9)—C(8)—H(8)	120.6 ± 1.2

Electron density and difference syntheses were calculated in the mean molecular plane defined by the ten carbon atoms (Table 6, plane 1) using the method of Damiani, Giglio & Ripamonti (1967) programmed for the IBM 1130 computer (Ammon, 1968). The electron density synthesis is shown in Fig. 2. The most striking feature of the difference map was a maximum of *ca.* 0.1 e.Å⁻³ at the center of each carbon-carbon bond whereas similar regions for the two carbon-oxygen bonds were essentially flat. These features are qualitatively the same as those found by Hirshfeld & Rabinovich (1967) for 2,5-dimethyl-1,4-benzoquinone (DMBZQ). Further analysis of the electron densities was not attempted.

The average C-C bond distance in the benzene ring, 1.392 Å (uncorrected, 1.387 Å), is close to the value found in benzene. Reasons for the somewhat short C(5)-C(6) and C(6)-C(7) distances are not clear. Other than the fused ring bond, C(9)-C(10), which resembles the benzene C-C bond, the distances in the quinoid ring are in reasonable agreement with the corresponding values observed in other quinones, for example 1,4-benzoquinone (Trotter, 1960), 2,3,5,6-tetrachloro-1,4-benzoquinone (Chu, Jeffrey & Sakurai, 1962) and 2,3,5,6-tetrahydroxy-1,4-benzoquinone (Klug, 1965).

The agreement of molecular parameters common to both DNQ and the well-determined DMBZQ is remarkable; the C(2) naphthoquinone substituent in DNQ apparently has the same structural effect as the methyl substituent in DMBZQ. A comparison of these features is readily made by reference to Table 5. Of special note are the well defined bond length differences between the C(sp²)-C(sp²) single bonds with three and with four substituents [C(3)-C(4) and C(1)-C(2) respectively].

Table 5. A comparison of structural parameters common to 2,2'-di(1,4-naphthoquinone) and 2,5-dimethyl-1,4-benzoquinone*

Bond or angle	DNQ	DMBZQ
C(1)-C(2)	1.501 Å	1.502 Å
C(2)-C(3)	1.340	1.347
C(3)-C(4)	1.483	1.482
C(1)-O(1)	1.220	1.223
C(4)-O(2)	1.224	
C(1)-C(2)-C(3)	120.2°	119.2°
C(2)-C(3)-C(4)	123.2	122.3
C(2)-C(1)-C(9)	117.8	118.5
C(3)-C(4)-C(10)	117.9	

* Hirshfeld & Rabinovich, 1967.

The C(2)-C(2') bond length of 1.492 Å is slightly greater than the value of 1.476 Å suggested as the normal C(sp²)-C(sp²) bond distance (Dewar & Schmeising, 1959). This difference may in part arise from the fact that the double bonds at C(2) and C(2') are twisted out of the planar *trans* arrangement by about 47°.

The average of the five uncorrected C(sp²)-H bond distances, 0.978 Å, is about 0.1 Å shorter than the spectroscopic value and in excellent agreement with the

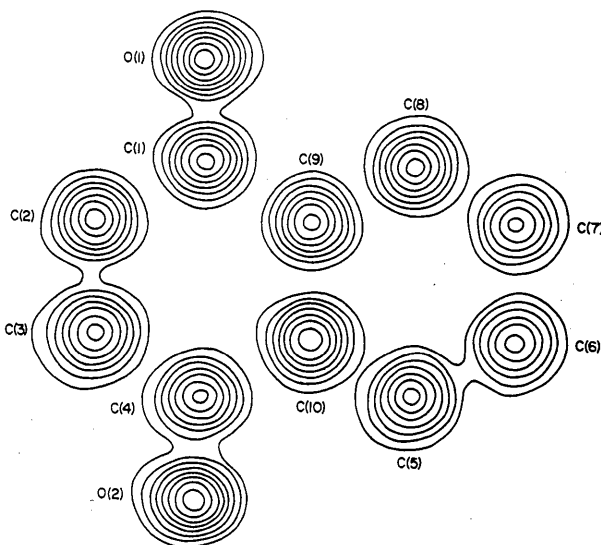


Fig. 2. Electron density synthesis evaluated in the mean molecular plane of the ten carbon atoms. Contours are drawn at intervals of 1 e.Å⁻³, with the lowest contour at 1 e.Å⁻³.

X-ray values observed for several recently reported structures (see Table 6, Stewart *et al.* 1965). An examination of the estimated standard deviations in the C-H and C-C bonds in this and several other structures points to the fact that $\sigma_{\text{C-H}} \approx 10\sigma_{\text{C-C}}$. This relation may be used to predict the best possible standard deviation obtainable for the hydrogens, knowing those of the carbons (or nitrogens/oxygens). It may be noted that in DNQ the hydrogen parameters (positional and isotropic temperature factors) and the carbon and oxygen parameters (positional and anisotropic temperature factors) were refined simultaneously, and the resulting C-H bond distances show no difference from those values obtained in refinements where the hydrogens and the 'heavy' atoms were refined separately. When thermal motion corrections are applied to the C-H bond distances, assuming a 'riding motion' of hydrogen upon carbon (Busing & Levy, 1964), the corrected C-H distances are still slightly less than the spectroscopic value.

The CCC and CCH bond angles involving the benzene ring are normal, but the CCC angles of the quinone ring show large variations. A contraction of the internal angles at the carbonyl carbons, average 119.9° in DNQ, has been observed in many quinones and other compounds with carbonyl groups. An increase in the internal angle at C(2) by 3° over that observed for C(3) is attributable to the presence of a substituent on C(2) and to the absence of one on C(3). This feature is also seen in other 2-substituted quinones, for example DMBZQ and 2-bromo-1,4-naphthoquinone (Gaultier & Hauw, 1965*b*). The external angle, C(1)-C(2)-C(2'), is 4.4° smaller than the C(3)-C(2)-C(2') angle, a feature which decreases the distance between the 2-substituent and the adjacent carbonyl oxygen and which has been also observed in other quinones

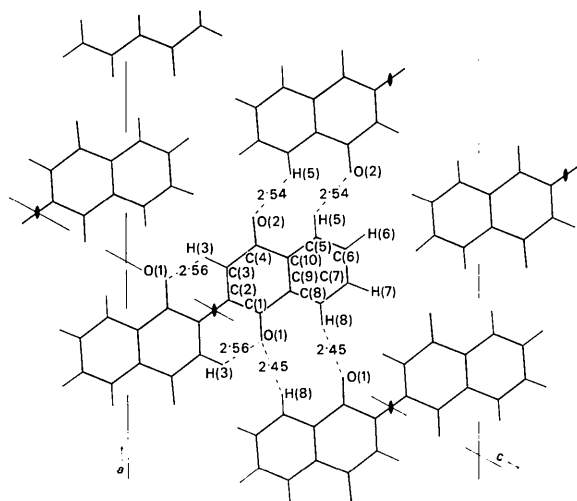


Fig. 3. Part of the crystal structure viewed along the *b* axis. Some intermolecular contacts (Å) are shown.

Table 6. *Least-squares planes (1) through all ten carbon atoms; (2) through the six carbon atoms of the benzene ring*

	Deviation (Å)	
	Plane 1	Plane 2
C(1)	-0.029	-0.044*
C(2)	0.010	0.003*
C(3)	0.000	0.007*
C(4)	0.015	0.029*
C(5)	-0.014	-0.001
C(6)	-0.012	-0.006
C(7)	0.015	0.007
C(8)	0.013	-0.001
C(9)	0.001	-0.006
C(10)	0.000	0.007
O(1)	-0.121*	-0.147*
O(2)	0.056*	0.083*
H(3)	-0.015*	-0.002*
H(5)	-0.015*	0.008*
H(6)	-0.023*	-0.012*
H(7)	-0.026*	-0.039*
H(8)	0.005*	-0.019*
R.m.s. deviation	0.015	0.006

* Asterisks indicate atoms which were not used to define the least-squares planes.

Equation of plane 1:

$$0.7821x + 0.3312y - 0.5379z = 1.$$

Equation of plane 2:

$$0.7576x + 0.3395y - 0.5410z = 1.$$

The planes were calculated according to the method of Schomaker, Waser, Marsh & Bergman (1959).

[e.g. DMBZQ and 2-methyl-3-hydroxy-1,4-naphthoquinone (Gaultier & Hauw, 1965*c*)]. The C-C-O(1) angles are identical within experimental errors while the C-C-O(2) angles differ by 3.4° .

Intra and intermolecular distances and planarity of the naphthoquinone ring

A steric interaction of O(1) and H(3) on one naphthoquinone half with H(3) and O(1) on the other half has resulted in a 47.3° twist about the C(2)-C(2') bond. The resultant H(3)···O(1) distances of 2.54 Å (Fig. 3) are precisely the values expected for normal van der Waals contact (*ca.* 2.6 Å) between hydrogen and oxygen. A similar H···O separation of 2.54 Å is observed between O(2) and H(5) at *x*, *y*, *z* and their respective counterparts at $\frac{1}{2}-x$, $-\frac{1}{2}-y$, $1-z$. The C(5)-H(5)···O(2) angle is far from linear (137.8°) and the assumption of the spectroscopic value of 1.075 Å for the C-H distances decreases this nonbonded contact to 2.46 Å.

The 2.45 Å intermolecular separation between O(1) and H(8) at *x*, *y*, *z* and the corresponding atoms at $-x$, $1-y$, $1-z$ represents a relatively strong C-H···O hydrogen bond. The C-H···O angle is 164.1° and an intermolecular distance of 2.33 Å is calculated using a C-H distance of 1.075 Å. Gaultier & Hauw (1966) have observed intermolecular O···H-C contacts of 2.40 and 2.45 Å for 2-methyl-3-amino-1,4-naphthoquinone.

Data for least-squares planes through the ten carbon atoms comprising the naphthoquinone nucleus and for the six atoms of the benzene ring are given in Table 6. The root-mean-square deviation from the ten atom plane is 0.015 Å; only O(1) and O(2) show significant deviations from the plane. A more dramatic view of possible molecular distortion can be had by considering the best plane through the six atoms of the benzene ring [C(5)–C(10)]. C(2) and C(3) are coplanar with the benzene ring while C(1), O(1) and C(4), O(2) have very significant and opposite deviations from the plane. This clearly shows that the quinone ring is distorted into the shape of a very shallow 'chair'.

It is difficult to assess the precise cause of the distortion. The deviation for O(1) is in a direction which relieves the O(1)···H(3) interaction (Fig. 3) but which increases the O(1)···H(8) interaction. The O(2) deviation is in a direction toward H(5). Surprisingly, the hydrogen atoms in question do not exhibit similar deviations from the least-squares planes.

The closest intermolecular contacts in the *b* direction are C(2)···O(1') = 3.47 Å and C(3)···O(1') = 3.40 Å, the prime referring to the naphthoquinone half at $-x, 1+y, \frac{1}{2}-z$.

Thermal movement

The results of a rigid body refinement (Cruickshank, 1956) for all twelve of the carbon and oxygen atoms and for only the ten carbon atoms are shown in Tables 7 and 8. An appreciable increase in ω_{33} is observed by inclusion of the two oxygens in the calculation. This is readily understood because the E_3 axis (to which ω_{33} refers) subtends an angle of 85° with the O(1)···O(2) line and the major axes of vibration (out of plane) of these two atoms deviate by no more than 6° from the normal to the naphthoquinone plane. The principle axes of the τ tensor show that the translational motion is essentially isotropic. The major axis of the ω tensor is almost parallel to the C(2)···C(6) line [normal to

the O(1)···O(2) line]. A torsional motion about the C(2)–C(2') bond should be the most facile mode for molecular libration.

One of us (HLA) wishes to express his gratitude to Drs Jerome and Isabella Karle for their hospitality and for the use of an automatic diffractometer. We are

Table 8. Principal axes of the τ and ω tensors relative to the set of orthogonal molecular axes*

For the 10 carbon and 2 oxygen atoms			
R.m.s. amplitude of translation (Å)	Direction angles (°)		
	<i>x</i>	<i>y</i>	<i>z</i>
0.17	127.2	79.0	33.4
0.20	129.4	134.6	108.8
0.17	118.8	46.8	123.1
R.m.s. angular oscillation (°)			
2.36	78.1	89.7	11.9
5.74	8.10	9.3	92.2
3.24	164.9	80.7	78.3
For the 10 carbon atoms			
R.m.s. amplitude of translation (Å)	Direction angles (°)		
	<i>x</i>	<i>y</i>	<i>z</i>
0.17	140.7	51.2	84.8
0.20	56.4	53.1	54.8
0.18	107.9	119.8	35.7
R.m.s. angular oscillation (°)			
2.62	126.0	85.5	143.6
4.43	85.2	5.2	88.0
3.04	143.6	87.3	53.7

* The molecular axes were defined in the following manner: *z* is the normal to the least-squares plane of the molecule ($z = 0.0079a + 0.2427b - 0.0161c$). *x* is perpendicular to *z* and the vector $0.1729a + 0.1371b + 0.3320c$ (this is the vector connecting C(2) and C(6)) and $y = z \times x$. *y* is virtually the same as the C(2)–C(6) vector.

Table 7. The τ (10^{-2} Å²) and ω (deg²) tensors, with estimated standard deviations, relative to the E^* axial system

For the 10 carbon and 2 oxygen atoms					
$\tau =$	$\begin{bmatrix} 2.89 & -0.06 & 0.01 \\ & 3.28 & 0.47 \\ & & 3.54 \end{bmatrix}$	$\sigma(\tau) =$	$\begin{bmatrix} 0.13 & 0.14 & 0.11 \\ & 0.21 & 0.13 \\ & & 0.12 \end{bmatrix}$		
$\omega =$	$\begin{bmatrix} 14.17 & 4.96 & 8.37 \\ & 6.10 & 3.22 \\ & & 28.83 \end{bmatrix}$	$\sigma(\omega) =$	$\begin{bmatrix} 1.56 & 1.06 & 0.96 \\ & 1.07 & 1.16 \\ & & 1.68 \end{bmatrix}$		
For the 10 carbon atoms					
$\tau =$	$\begin{bmatrix} 2.89 & 0.10 & -0.03 \\ & 3.76 & 0.33 \\ & & 3.57 \end{bmatrix}$	$\sigma(\tau) =$	$\begin{bmatrix} 0.14 & 0.15 & 0.11 \\ & 0.26 & 0.13 \\ & & 0.11 \end{bmatrix}$		
$\omega =$	$\begin{bmatrix} 11.56 & 1.43 & 4.34 \\ & 7.29 & 1.41 \\ & & 16.87 \end{bmatrix}$	$\sigma(\omega) =$	$\begin{bmatrix} 1.74 & 1.17 & 1.71 \\ & 1.25 & 1.88 \\ & & 4.65 \end{bmatrix}$		

* The Patterson (1952) orthogonal E vector system. The rigid body refinement was calculated with the program DIAGUS (Stewart, 1966).

also grateful to the Research Committee, University of California at Santa Cruz; the Computer Science Center, University of Maryland (grant no. NSG-398) and the United States Public Health Service (grant no. GM-14828) for financial support.

References

- ALEXANDER, L. E. & SMITH, G. S. (1964). *Acta Cryst.* **17**, 1195.
- AMMON, H. (1968). *FIRST: A Program for the Evaluation of a Fourier Synthesis in a General Plane for the IBM 1130*. Unpublished work.
- BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.
- BUSING, W. R. & LEVY, H. A. (1964). *Acta Cryst.* **17**, 142.
- CHU, S., JEFFREY, G. A. & SAKURAI, T. (1962). *Acta Cryst.* **15**, 661.
- CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 754.
- DAMIANI, A., GIGLIO, E. & RIPAMONTI, A. (1967). *Acta Cryst.* **22**, 692.
- DEWAR, M. J. S. & SCHMEISING, H. N. (1959). *Tetrahedron*, **5**, 166.
- GAULTIER, J. & HAUW, C. (1965a). *Acta Cryst.* **18**, 179.
- GAULTIER, J. & HAUW, C. (1965b). *Acta Cryst.* **18**, 604.
- GAULTIER, J. & HAUW, C. (1965c). *Acta Cryst.* **19**, 919.
- GAULTIER, J. & HAUW, C. (1966). *Acta Cryst.* **21**, 694, and references therein.
- HAND, E. S. & COHEN, T. (1967). *Tetrahedron*, **23**, 2911.
- HIRSHFELD, F. L. & RABINOVICH, D. (1967). *Acta Cryst.* **23**, 989.
- HUGHES, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737.
- KARLE, I. L. & BRITTS, K. (1966). *Acta Cryst.* **21**, 532.
- KLUG, H. P. (1965). *Acta Cryst.* **19**, 983.
- PATTERSON, A. L. (1952). *Acta Cryst.* **5**, 829.
- PROUT, C. K. & WALLWORK, S. C. (1966). *Acta Cryst.* **21**, 449.
- PUMMERER, R., PFAFF, A., TIEGELBAUER, G. & ROSENHAUER, E. (1939). *Ber. dtsh chem. Ges.* **72**, 1623.
- ROSENHAUER, E., BRAUN, F. & PUMMERER, R. (1937). *Ber. dtsh chem. Ges.* **70**, 2281.
- SCHOMAKER, V., WASER, J., MARSH, R. E. & BERGMAN, G. (1959). *Acta Cryst.* **12**, 600.
- STEWART, R. F. (1966). *DIAGUS: Principal Directions of Thermal Ellipsoids and Rigid Body Analysis*. Unpublished work.
- STEWART, R., DAVIDSON, E. & SIMPSON, W. (1965). *J. Chem. Phys.* **42**, 3175.
- SUNDARALINGAM, M. (1961). *Acta Cryst.* **14**, 894.
- TROTTER, J. (1960). *Acta Cryst.* **13**, 86.
- X-ray 63 *Crystal Structure Calculations System*, TR-64-6 (NSG-398), Computer Science Center, University of Maryland, and Research Computer Center, University of Washington.

Acta Cryst. (1969). B25, 343

The Crystal and Molecular Structure of Thiosemicarbazide

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(Received 6 November 1967)

The crystal structure of thiosemicarbazide, $\text{SC}(\text{NH}_2)\text{NHNH}_2$, has been determined by a three-dimensional X-ray analysis and refined both by differential and least-squares methods, using anisotropic thermal parameters: final $R=9.9\%$. The crystals are triclinic (PT): $a=4.911(5)$, $b=7.127(7)$, $c=8.340(7)$ Å, $\alpha=45^\circ 28'(3')$, $\beta=83^\circ 50'(3')$, $\gamma=77^\circ 34'(3')$, $Z=2$. The arrangement of the non-hydrogen atoms is nearly planar, with the S and the hydrazinic NH_2 group in a *trans* position with respect to the C-NH bond. Bond distances and angles are: C-S=1.685(5), C-N(1)=1.313(6), C-N(2)=1.337(6), N(2)-N(3)=1.399(6) Å, SCN(1)=119.7°(3), SCN(2)=121.5°(3), N(1)CN(2)=118.8°(4), CN(2)-N(3)=122.5°(4). The nitrogen atom, N(3), of the hydrazinic NH_2 group is 0.04 Å out the plane through the thiourea part of the molecule.

Introduction

Thiosemicarbazide behaves as a bidentate ligand with conformation (I) in monomeric metal complexes: e.g. dichloromonothiosemicarbazidezinc (Cavalca, Nardelli & Branchi, 1960), bithiosemicarbazidonickel(II) (Cavalca, Nardelli & Fava, 1962), *trans*-bithiosemicarbazidenickel(II) sulphate trihydrate (Grønbaek & Rasmussen, 1962), α and β forms of bithiosemicarbazidenickel(II) sulphate (Grønbaek, 1963), trithiosemicarbazidenickel(II) dinitrate and bithiosemicarbazidenickel(II) dinitrate dihydrate (Grønbaek Hazell,

1966). In the polymeric monochloromonothiosemicarbazidesilver (Nardelli, Fava Gasparri, Giraldi Battistini & Musatti, 1965) its conformation is (II) with a monodentate behaviour.

