with the more definitive bond distances available from neutron diffraction studies of carbohydrates (*cf.* Jeffrey, Gress & Takagi, 1977). The corrected H···O distances for hydrogen bonds between the hydroxyl groups range from 1·75 to 1·88 Å. This is intermediate between the 1·736 to 1·820 Å range observed in the neutron diffraction studies of the monosaccharides [methyl α-D-manno- and methyl α-D-glucopyranoside (Jeffrey, McMullan & Takagi, 1977); α-D-glucose (Brown & Levy, 1965)], and 1·760 to 1·927 Å in the disaccharides [sucrose (Brown & Levy, 1973); β-maltose monohydrate (Gress & Jeffrey, 1977)]. This could be a consequence of the fact that from the point of view of packing, these molecules have the complexity of a disaccharide, with the acyclic half of the molecule more flexible than in sucrose or maltose. The hydrogen bond to the ring oxygen is longer than between two hydroxyls, but the difference is not as marked as in the methyl pyranoside data referred to above.

This research has been performed under the auspices of the US Energy Research and Development Administration and supported by NIH Research Grant GM-21794.

References

Arnott, S. & Scott, W. E. (1972). *J. Chem. Soc. Perkin* II, pp. 324–335.

Brown, G. M. & Levy, H. A. (1965). *Science*, **147**, 1038.

Brown, G. M. & Levy, H. A. (1973). *Acta Cryst.* B**29**, 790–797.

Coppens, P. & Hamilton, W. C. (1970). *Acta Cryst.* A**26**, 70–83.

Cremer, D. & Pople, J. (1975). *J. Amer. Chem. Soc.* **97**, 1354–1358.

Doyle, P. A. & Turner, P. S. (1968). *Acta Cryst.* A**24**, 390–397.

Gatehouse, B. M. & Poppleton, B. J. (1971). *Acta Cryst.* B**27**, 654–660.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

Gress, M. & Jeffrey, G. A. (1977). *Acta Cryst.* In the press.

Jeffrey, G. A., Gress, M. & Takagi, S. (1977). *J. Amer. Chem. Soc.* **99**, 609–611.

Jeffrey, G. A., McMullan, R. K. & Takagi, S. (1977). *Acta Cryst.* B**33**, 728–737.

Jeffrey, G. A., Pople, J. A. & Radom, L. (1972). *Carbohydr. Res.* **25**, 117–131.

Jeffrey, G. A., Pople, J. A. & Radom, L. (1974). *Carbohydr. Res.* **38**, 81–95.

Jeffrey, G. A. & Takagi, S. (1977). *Acta Cryst.* B**33**, 738–742.

Johnson, C. K. (1976). *ORTEP* II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.

Longchambon, P. F., Ohannessian, J. & Neuman, D. A. A. (1975). *Acta Cryst.* B**31**, 2623–2627.

Sheldrick, B. (1976). *Acta Cryst.* B**32**, 1016–1020.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Stoddart, J. F. (1971). *Stereochemistry of Carbohydrates*. New York: John Wiley.

Templeton, L. K. & Templeton, D. H. (1973). Amer. Cryst. Assoc. Meeting, Storrs, Connecticut. Abstract *E*10.

Acta Cryst. (1977). B**33**, 2380–2384

Molecular-Packing Analysis of Some Naphthaquinone and Anthraquinone Structures. The Crystal Structure of 2-Methyl-5,8-dihydroxy-1,4-naphthaquinone

By Peter D. Cradwick, David Hall and Murray K. Wood

Chemistry Department, University of Auckland, Auckland, New Zealand and Chemistry Department, University of Alberta, Edmonton, Alberta, Canada

(*Received* 19 *July* 1976; *accepted* 19 *January* 1977)

The structures corresponding to a minimum non-bonded repulsion energy have been shown to be in close agreement with the observed structures for a number of naphthaquinones and anthraquinones. The previously unknown structure of 2-methyl-5,8-dihydroxy-1,4-naphthaquinone was successfully predicted with this procedure. [Crystal data: $C_{11}H_8O_4$, triclinic, $a = 7{\cdot}431$ (2), $b = 8{\cdot}479$ (2), $c = 16{\cdot}654$ (3) Å, $\alpha = 87{\cdot}31$ (5), $\beta = 106{\cdot}8$ (1), $\gamma = 114{\cdot}5$ (2)°, $Z = 4$.]

Introduction

The procedure developed by Williams (1969) for the prediction of molecular crystal structure by the minimization of non-bonded, repulsive packing energy assumes implicitly that the structure is not dominated by specific attractive interactions between molecules. It is, then, essentially applicable to non-polar molecules, but because this procedure is very much faster in terms of computer time than packing-analysis techniques which do include attractive terms, it was of interest to investigate its applicability to molecules containing polar groupings. This paper reports studies on structures of naphthaquinones, anthraquinones and some hydroxyl-substituted quinones.

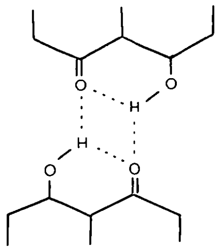
Packing analysis

Packing calculations were made with the program *PCK5* (Williams, 1969), in which the repulsive energy of interaction between two atoms of different molecules is given by $\varepsilon_r = \omega(d_o - d)^2$, $d < d_o$; $\varepsilon_r = 0$, $d > d_o$, where d is the interatomic distance, d_o that interatomic distance corresponding to the minimum of the corresponding non-bonded potential-energy curve, and ω is a weighting constant. The repulsive lattice energy is calculated as $2E_r = \Sigma\ \varepsilon_r$, where the summation is over all contacts between atoms of the reference molecule and atoms of surrounding molecules. From a given starting model, repulsive lattice energy is minimized with respect to rigid-body molecular parameters, the lattice constants and the symmetry being assumed to be known. The constants d_o and ω for a particular atom pair can be obtained by a least-squares fit to the appropriate (exp − 6) potential curve (Williams, 1969), or by an empirical fit to known structures; the values used in this study are listed in Table 1, being those given by Williams for C—C, C—H and H—H interactions, and empirically determined values for interactions involving O atoms.

The starting model in each case was the molecule as defined by the published coordinates for non-hydrogen atoms, with H atoms in positions calculated for the expected geometry with C—H 1·027 Å (Williams, 1965), and O—H 0·95 Å. After refinement to minimum energy the difference between the initial and the refined coordinates was expressed as $\varphi = (\Sigma_{i,N} \Delta^2_{i,N}/3N)^{1/2}$, where Δ_i is the difference in the ith Cartesian coordinate of each of the N atoms of the molecule (Zugenmaier & Sarko, 1972). These values together with the corresponding values of the minimum E_r are listed in Table 2 for some hydrocarbon structures (for reference), and for the quinone and hydroxyl-substituted quinone structures of this study. The latter were specifically chosen as being molecules in which intramolecular hydrogen bonds form, and thus the structures might be expected not to be dominated by intermolecular hydrogen bonds. In those cases indicated by an asterisk in Table 2, both inter- and intramolecular bonds exist, as in (I). The effect of this was that the O—H contacts manifested themselves as repulsions, when they are of course just the opposite. For these structures the hydrogen-bonded parameters of Table 1 were adopted, the reduced value of d_o ensuring that even though the analysis ignores the attractive contribution of the intermolecular hydrogen bond, at least this bond does not incur a penalty. For the methyl-substituted molecules it was found that the packing energy was not greatly affected by the particular rotational conformation adopted for the methyl

Table 1. *Potential parameters*

Interaction	d_o (Å)	w (kcal mol^{-1} Å^{-2})
C···C	3·65	1·87
C···H	3·03	1·56
H···H	2·88	1·00
C···O	3·4	1·0
H···O	3·0	1·2
O···O	3·2	1·2
H···O } Hydrogen	2·3	2·0
O···O } bonded	2·8	2·0



(I)

Table 2. *Results of energy minimization, starting with the observed structure*

	φ(Å)	$2E_r$ (kcal)	References
Benzene	0·04	0·76	1
Naphthalene	0·04	0·77	2
Phenanthrene	0·08	1·24	3
1,4-Naphthaquinone	0·04	1·50	4
2,3-Dimethyl-1,4-naphthaquinone	0·05	1·49	5
3-Phenyl-1,4-naphthaquinone	0·06	1·87	6
2,3-Dihydro-2,3-methylene-1,4-naphthaquinone	0·02	0·51	7
9,10-Anthraquinone	0·01	1·40	8
p-Benzoquinone	0·30	0·62	9
*5-Hydroxy-1,4-naphthaquinone	0·35	1·45	10
2-Methyl-3-hydroxy-1,4-naphthaquinone	0·17	1·58	11
†Naphthazarin *A*	0·20	0·52	12
†Naphthazarin *B*	0·28	1·14	13
*†Naphthazarin *C*	0·12	1·39	12
1,8-Dihydroxy-9,10-anthraquinone	0·05	1·83	14
*1,5-Dihydroxy-9,10-anthraquinone	0·14	2·81	15

References: (1) Bacon, Curry & Wilson (1964). (2) Cruickshank (1957). (3) Trotter (1963). (4) Gaultier & Hauw (1965). (5) Breton-Lacombe (1967). (6) Courseille, Gaultier & Hauw (1969). (7) Grant & Speakman (1962). (8) Lonsdale, Milledge & El Sayed (1966). (9) Trotter (1960). (10) Cradwick & Hall (1971*a*). (11) Gaultier & Hauw (1966). (12) Cradwick & Hall (1971*b*). (13) Pascard-Billy (1962). (14) Prakash (1965). (15) Hall & Nobbs (1966).

* Intermolecular hydrogen-bonded structure.

† Naphthazarin (formally 5,8-dihydroxy-1,4-naphthaquinone) exists in three crystalline modifications.

group, but that φ was more sensitive (*e.g.* φ varied between 0·06 and 0·24 in the case of 2,3-dimethyl-1,4-naphthaquinone), and the optimum rotational conformation of the methyl groups was established by trial.

It may be seen from Table 2 that the structures of the simple naphtha- and anthraquinones are described by the minimum-repulsion model as effectively as are the hydrocarbon structures, and it appears that interactions between the carbonyl dipoles are not of particular importance in defining the structures. It is, however, notable that for *p*-benzoquinone, in which the carbonyls are a more dominant feature, the difference between the observed structure and that of the energy minimum is distinctly greater. For the hydroxyquinone structures the φ values are higher, but in all cases the energy-minimum model is well within the range that would enable it to be the starting point of a structure refinement based on X-ray data. To confirm that packing analysis could indeed be a feasible method for structure solution for such molecules, the various repulsion-energy minima over the domain described by the rigid-body parameters were located, as described by Williams (1969), for several of the molecules of Table 1. Only the cell parameters, space group, number of molecules in the cell, and the idealized molecular dimensions were assumed. The examples chosen were anthraquinone and naphthazarin *B* (for which only rotational parameters need be determined) and 1,4-naphthaquinone and 2,3-dimethyl-1,4-naphthaquinone (which require translational parameters as well). In each case there were various false minima, very many of them in the six-dimensional spaces, but in each the lowest energy minimum was indeed that described in Table 1.

The structure of 2-methyl-5,8-dihydroxy-1,4-naphthaquinone

The procedure was then applied to predict the unknown structure of a methyl derivative of naphthazarin, which turned out to be 2-methyl-5,8-dihydroxy-1,4-naphthaquinone, although at the time the position of methyl substitution was unknown. Dark-red crystals had been prepared by a Friedel–Crafts reaction between methylhydroquinone and maleic anhydride, and recrystallized from glacial acetic acid. Crystal data are: $C_{11}H_8O_4$, triclinic, $a = 7{\cdot}431\ (2)$, $b = 8{\cdot}479\ (2)$, $c = 16{\cdot}654\ (3)$ Å, $\alpha = 87{\cdot}31\ (5)$, $\beta = 106{\cdot}8\ (1)$, $\gamma = 114{\cdot}5\ (2)°$, $Z = 4$, $D_m = 1{\cdot}51$, $D_c = 1{\cdot}49$ g cm^{-3}.

Even if space group $P\bar{1}$ is assumed there are two independent molecules in the asymmetric unit. Intensity data were collected on a Pailred diffractometer, with crystal-monochromatized Cu $K\alpha$ radiation, for the layers $0kl$–$4kl$. Of 2350 reflexions scanned, 1693 had $I > 2\sigma(I)$ and were deemed to be observed. From an analysis of the Patterson function it was deduced that both molecules are parallel to (100), either both in section $x = \frac{1}{4}$, or one at $x = 0$ and one at $x = \frac{1}{2}$, with the molecules oriented so that the C=O bond vectors of the two molecules make angles of +30° and −30° respectively with **b**. The complexity of the intermolecular vector system was, however, such that numerous attempts at interpretation failed to yield a refinable structure. Attempts at a solution by direct phasing methods also proved unsuccessful.

In the initial stage of the packing investigation the methyl group was not included in the model, and the naphthazarin residue was assumed to have D_{2h} symmetry. With the information from the Patterson analysis there remain four parameters to be established (in addition to resolving the ambiguity in the x coordinate). In fact the latter was relatively simple; the density of centres of inversion on sections $x = 0$ and $\frac{1}{2}$ is such that the molecules can only be positioned with molecular centre near $(x,\frac{1}{4},\frac{1}{4})$ or equivalent positions, and none of the possible combinations led to an acceptable structure. On $x = \frac{1}{4}$ there is no such restriction. Starting models for refinement were generated by moving the molecular centres of the two molecules independently over a 2 Å grid, eliminating only those for which the distance between centres was less than 6 Å. There were 230 non-equivalent such models, each of which was refined with respect to the four unknown parameters. Somewhat disconcertingly this led to 87 distinct solutions for which E_r varied from 13·37 to 17·75 kcal. It was clear from the energy values that the constraints as deduced from the Patterson analysis were too restrictive, but within these constraints the more or less circular outline of the idealized molecule allowed many arrangements to be equally efficient. The molecular constraints were relaxed in stages, and the above solutions refined finally with respect to all 12 rigid-body parameters. There then remained 46 distinct solutions for the packing of the naphthazarin residue, with E_r ranging from 1·06 to 2·60 kcal. Since there are four possible points of attachment of the methyl group in each molecule, there are 16 arrangements of the methyl groups, corresponding to each of these solutions. Starting from that of lowest energy, all 16 methylnaphthazarin structures were refined with respect to the 12 rigid-body parameters, the values of E_r thus obtained ranging from 2·94 to 7·5 kcal. Those methylnaphthazarin structures for which E_r was less than 3·2 kcal were tested against the set of 46 X-ray data with $\sin\theta/\lambda < 0{\cdot}16$, and refined by least squares against these data with respect to the rigid-body parameters. Several models returned R indices of 0·54–0·60 before one refined to 0·28, and this structure thereafter was successfully refined against the full set of X-ray data. Refinement was by full-matrix least squares, with anisotropic thermal motion for C and O atoms. The function minimized was $\Sigma\, w(F_o - F_c)^2$, where $w = (a + b|F_o| + c|F_o|^2)^{-1}$, a, b and c being chosen such that $\langle w|F_o|^2\rangle$ was invariant with $|F|$. The

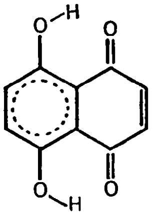
Table 3. *Atom coordinates*

	x (×10³)	y (×10³)	z (×10⁴)
C(1)	255 (2)	−223 (1)	157 (5)
C(2)	229 (2)	−133 (1)	−576 (5)
C(3)	254 (2)	−385 (1)	50 (6)
C(4)	204 (2)	−208 (1)	−1369 (6)
C(5)	232 (2)	−458 (1)	−766 (6)
C(6)	202 (2)	−374 (1)	−1452 (6)
C(7)	259 (2)	110 (1)	366 (6)
C(8)	280 (2)	28 (1)	1070 (6)
C(9)	284 (2)	−146 (1)	979 (6)
C(10)	234 (2)	40 (1)	−469 (6)
C(11)	303 (2)	100 (2)	1955 (7)
O(1)	286 (2)	−475 (1)	716 (4)
O(2)	187 (1)	−125 (1)	−2066 (4)
O(3)	218 (1)	126 (1)	−1090 (4)
O(4)	307 (1)	−221 (1)	1635 (4)
C(21)	259 (2)	559 (1)	5142 (5)
C(22)	239 (2)	456 (1)	4414 (5)
C(23)	256 (2)	487 (1)	5962 (5)
C(24)	218 (2)	277 (1)	4483 (6)
C(25)	235 (2)	305 (1)	6014 (6)
C(26)	219 (2)	213 (1)	5331 (6)
C(27)	264 (2)	699 (1)	3588 (6)
C(28)	279 (2)	796 (1)	4272 (6)
C(29)	277 (2)	728 (1)	5070 (6)
C(30)	244 (2)	527 (1)	3633 (5)
C(31)	233 (2)	236 (1)	6880 (6)
O(21)	267 (1)	573 (1)	6596 (4)
O(22)	206 (1)	185 (1)	3872 (4)
O(23)	231 (1)	438 (1)	2935 (4)
O(24)	286 (1)	830 (1)	5728 (4)

data were not of high accuracy, and although on a final difference synthesis the H atoms attached to C atoms were recognizable, there were background peaks of comparable height, and the hydroxyl H atoms were not discernible. The final R, with the located H atoms included with isotropic temperature factors, was 0·104.* Coordinates of atoms other than H are listed in Table 3, and bond lengths and the atom-numbering scheme are shown in Fig. 1. The arrangement of molecules in the unit cell is shown in Fig. 2.

The correct structure corresponded to the second-lowest packing-energy minimum for a methyl-naphthazarin structure, for which E_r was 2·96 kcal. The rotational conformation of the methyl groups had been chosen arbitrarily for the initial model; when these angles were optimized the E_r value was 2·83 kcal, the lowest value for any model tested. The φ value was relatively high at 0·32, but, as reported, the refinement based on X-ray data proceeded without difficulty. The existence of independent molecules in a low-symmetry structure made this a difficult problem, yet it was solved, and it appears that more extensive use of packing analysis as a structure-solving technique may well be justified.

Interest in the crystal structure of 2-methyl-5,8-dihydroxy-1,4-naphthaquinone is related to that of naphthazarin (II), which has been the subject of numerous structural studies (Cradwick & Hall, 1971*b*, and references therein). There are three crystalline modifications, in each of which the molecule is apparently centrosymmetric, and thus unless the structures are disordered formula II cannot be correct. The methyl derivative was prepared in order to break the symmetry or pseudosymmetry of the molecule, and it may be seen from the bond lengths of Fig. 1 that in each of the independent molecules this compound does possess distinct quinonoid and phenolic rings, with the methyl group attached to the former, and thus it is indeed the 2-methyl derivative of (II). The point of methyl substitution was not previously known. A comparison



(II)

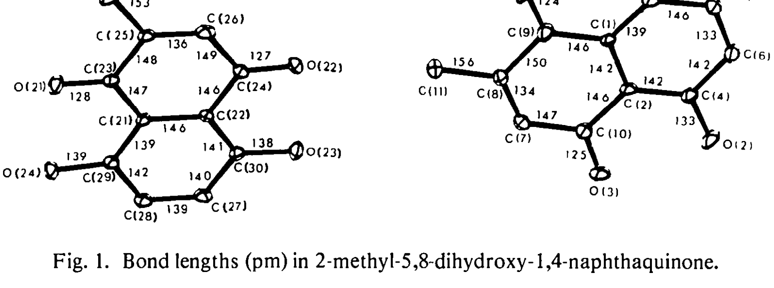


Fig. 1. Bond lengths (pm) in 2-methyl-5,8-dihydroxy-1,4-naphthaquinone.

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32461 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

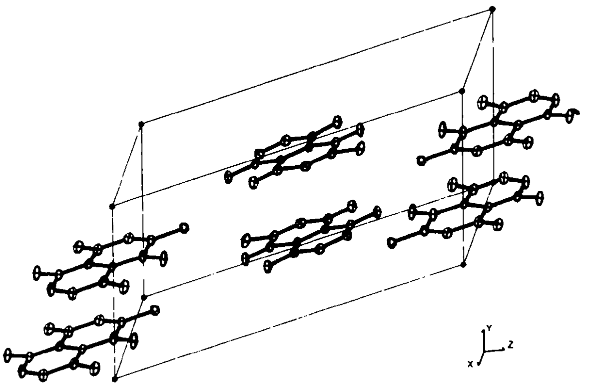


Fig. 2. The packing arrangement of the molecules.

of the lengths of different bond types with those observed in 9,10-anthraquinone (Lonsdale, Milledge & El Sayed, 1966) and 1,5-dihydroxy-9,10-anthraquinone (Hall & Nobbs, 1966) (two similar compounds which have been studied accurately) shows them to be generally in good agreement. Each molecule possesses a planar naphthalene residue with maximum deviations from the mean planes of 0·022 and 0·011 Å respectively (σ = 0·014 Å); some of the substituent atoms are displaced as much as 0·05 Å from coplanarity. There are no intermolecular O···O contacts less than 3·3 Å, and thus the hydrogen bonding is solely intramolecular.

We are indebted to Professor D. E. Williams for providing the program *PCK*5, and for valuable discussions relating to the procedures used.

References

Bacon, G. E., Curry, N. A. & Wilson, S. A. (1964). *Proc. Roy. Soc.* A**279**, 98–110.

Breton-Lacombe, M. (1967). *Acta Cryst.* **23**, 1024–1031.

Courseille, C., Gaultier, J. & Hauw, C. (1969). *C. R. Acad. Sci. Paris*, **268**, 1358–1360.

Cradwick, P. D. & Hall, D. (1971*a*). *Acta Cryst.* B**27**, 1468–1470.

Cradwick, P. D. & Hall, D. (1971*b*). *Acta Cryst.* B**27**, 1990–1997.

Cruickshank, D. W. J. (1957). *Acta Cryst.* **10**, 504–508.

Gaultier, J. & Hauw, C. (1965). *Acta Cryst.* **18**, 179–183.

Gaultier, J. & Hauw, C. (1966). *Acta Cryst.* **19**, 919–926.

Grant, W. K. & Speakman, J. C. (1962). *Acta Cryst.* **15**, 292–293.

Hall, D. & Nobbs, C. L. (1966). *Acta Cryst.* **21**, 927–934.

Lonsdale, K., Milledge, H. J. & El Sayed, K. (1966). *Acta Cryst.* **20**, 1–13.

Pascard-Billy, C. (1962). *Bull. Soc. Chim. Fr.* pp. 2282–2293.

Prakash, A. (1965). *Z. Kristallogr.* **122**, 272–282.

Trotter, J. (1960). *Acta Cryst.* **13**, 86–95.

Trotter, J. (1963). *Acta Cryst.* **16**, 605–608.

Williams, D. E. (1965). *J. Chem. Phys.* **43**, 4424–4426.

Williams, D. E. (1969). *Acta Cryst.* A**25**, 464–470.

Zugenmaier, P. & Sarko, A. (1972). *Acta Cryst.* B**28**, 3158–3166.

Acta Cryst. (1977). B33, 2384–2388

The Crystal and Molecular Structure of a Bridged and Intramolecularly Alkylated Cobaloxime, $C_{25}H_{40}N_5O_4Co$

By W. Pannhorst

Institut für Kristallographie, Universität (*TH*) *Karlsruhe, Kaiserstrasse* 12, 7500 *Karlsruhe, Germany*

(*Received* 29 *November* 1976; *accepted* 25 *January* 1977)

$C_{25}H_{40}N_5O_4Co$ crystallizes in space group $P2_1/c$, with unit-cell dimensions a = 9·275 (3), b = 23·308 (6), c = 12·905 (4) Å, β = 114·29 (1)°, Z = 4. The atomic parameters were refined to a final R value of 0·073 for 2307 observed reflexions. The molecules, in which the bridge is arranged in the *cis* configuration, have no mirror plane.

Introduction

Bis(dimethylglyoximato)cobalt complexes, 'cobaloximes', have been used as model compounds for the more complex cobalamines (Schrauzer, 1968, 1971). Among the cobalamines the vitamin B_{12} coenzyme is of particular interest. Its structure was determined by Lenhert & Hodgkin (1961) and Lenhert (1968). Looking for better model compounds for the coenzyme B_{12} enzymatic reactions, Rétey (1971) synthesized bridged glyoxime cobalt complexes which, for convenience, will also be called cobaloximes. For one of these com-