

Effects of Packing on the Conformation of Obtusaquinone

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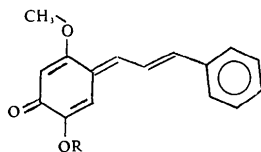
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Obtusaquinone, $C_{16}H_{14}O_3$, an orange pigment isolated from the *Dalbergia retusa* tree, crystallizes as a hydrogen-bonded dimer in space group $P2_1/a$ with $a=19.661$ (15), $b=9.722$ (5), $c=16.527$ (10) Å and $\beta=97.84$ (4)°. Each asymmetric unit contains two molecules of obtusaquinone (the dimeric unit) and one molecule of benzene. The dimers formed by the two independent molecules are related by a pseudo center of symmetry that does not coincide with a crystallographic symmetry center. Thus the statistical averages for the E values indicate a hypercentric cell. The decidedly bowed shape of each obtusaquinone molecule, as contrasted with the nearly planar conformation for the *O*-methyl derivative, appears to be related to packing forces. The molecules are stacked nearly parallel to each other with attractions between neighboring quinone moieties and repulsions between nearly parallel neighboring phenyl groups. The benzene molecules lie in continuous channels parallel to the a axis. The plane of the benzene molecule is inclined $\sim 70^\circ$ to the least-squares planes of the obtusaquinone molecules.

The wood of the tropical tree *Dalbergia retusa* Hemsl. (cocobolo), ranging from Panama to Nicaragua, has been found to be most resistant, among a large number of tropical woods tested, to biodegradation in the sea and on land (Southwell & Bultman, 1971, 1973). A phytochemical examination of the heartwood tissue for the purpose of isolating and identifying the protective constituent for possible use as an impregnant for conventional, coniferous woods yielded an orange pigment identified as obtusaquinone (*Ia*) (Jurd, Stevens & Manners, 1972). This compound is effective in protecting non-resistant pine against teredos (shipworms) and also against termites, including the voracious Asian species, *Coptotermes formosanus* (Bultman & Beal, unpublished). The compound affects the physiology of the borers by causing abnormal calcium metabolism.



(*Ia*) R = H
(*Ib*) R = CH₃

The crystal structure analysis of *O*-methylobtusaquinone established the structure as (*Ib*) (Palmer, Wong & Jurd, 1973). The present structure analysis of the native obtusaquinone shows that the molecule has the same stereoconfiguration as the *O*-methyl derivative, but that the molecules occur as hydrogen-bonded dimers (two molecules per asymmetric unit). The packing for the dimer is entirely different from the *O*-methyl derivative and causes the obtusaquinone molecules to assume decidedly bowed conformations.

Experimental

Obtusaquinone exists as a deep-red powder. Clear, deep-orange, elongated flat plates grown from benzene have an optical extinction along the long direction. The calculated crystal density suggested, and the structure analysis confirmed, that there are two molecules of obtusaquinone and one molecule of benzene per asymmetric unit. After several days, the diffracted intensity of the three monitored reflections decreased and the crystal began to show a dark-red opaque area. Eventually all the crystals (exposed and unexposed to X-rays) turned dark red and opaque although they maintained their exterior faces. It appears that the change in color and character may be correlated with the loss of benzene from the crystal lattice.

Cell parameters were determined by a least-squares fit to the θ , ω , ψ and φ values for 12 reflections centered on a four-circle automatic diffractometer. Intensity data were collected for all reflections with $2\theta \leq 90^\circ$ using a 2.0° scan over θ with a scan speed of $2^\circ/\text{min}$ and a background reading of 10 s at either end of the scan. Reflections at $2\theta > 90^\circ$ had very low intensities. Three reflections were monitored after every 50 measurements. The decrease in the values of the monitors was isotropic and the measured data were corrected for the decay, a maximum of 13% for the data measured last. Pertinent crystal data are: space group $P2_1/a$; $a=19.661 \pm 0.015$, $b=9.722 \pm 0.005$, $c=16.527 \pm 0.010$ Å, $\beta=97.84 \pm 0.04^\circ$; $V=3129.5$ Å³; Asym. unit $2(C_{16}H_{14}O_3) \cdot C_6H_6$; M.W./asym. unit 586.69; $d_{\text{calc}}=1.245$ g cm⁻³; $\lambda=1.54178$ Å; $\mu=6.93$ cm⁻¹; size $0.11 \times 0.90 \times 0.35$ mm; number of independent reflections, 2528. The statistical averages, $\langle |E| \rangle = 0.72$ and $\langle |E^2 - 1| \rangle = 1.13$, as compared to theoretical values for cen-

trosymmetric crystals, 0.798 and 0.968, respectively, indicate hyper-centering. This is, in fact, borne out in the structure since pseudo centers between the two independent molecules occur in the negative (40 $\bar{4}$) planes.

The structure was solved directly by the symbolic addition procedure (Karle & Karle, 1963). The first *E* map revealed the 38 atoms of the two obtusaquinone molecules. Least-squares refinement resulted in an *R* value of 36%, an indication that the structure was not complete. A difference map showed six weak peaks, 2.4 to 2.8 e Å³, in a planar hexagon which could correspond to a benzene molecule. Inclusion of the six

additional C atoms in the least squares lowered *R* to 19.5% for isotropic thermal factors and 12.1% for anisotropic thermal factors. The function minimized was $\sum w_F(F_o - F_c)^2$ where $w_F = 1/\sigma_F^2$ (as defined by Gilardi, 1973). All the data contained within the sphere with $2\theta \leq 90^\circ$, including those reflections with zero intensity, were used in the full-matrix least-squares refinement. A difference map indicated the positions of 28 H atoms; however, most of the C-H bond lengths were too long by 0.1–0.2 Å, although the values of the angles were satisfactory. Therefore the coordinates for 28 H atoms, for the obtusaquinone molecules, in calculated positions and with *B* = 5.0 were included as

Table 1. Fractional coordinates ($\times 10^4$) and thermal parameters for obtusaquinone

The thermal parameters are of the form $T = \exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> ₁₁	<i>B</i> ₂₂	<i>B</i> ₃₃	<i>B</i> ₁₂	<i>B</i> ₁₃	<i>B</i> ₂₃
C(1A)	3723	7694	2495	4.18	3.24	3.57	0.28	-0.24	-0.05
C(2A)	3241	8588	1981	5.42	2.02	4.62	-0.14	-0.48	-0.75
C(3A)	2696	8168	1471	5.24	1.47	3.60	-1.09	-1.15	-1.08
C(4A)	2571	6705	1399	3.94	3.54	3.81	0.31	-1.13	0.34
C(5A)	3057	5776	1888	4.55	2.50	3.80	0.07	-0.17	0.13
C(6A)	3605	6222	2394	4.66	1.09	4.49	-0.17	-1.02	0.09
C(7A)	4249	8279	3017	4.83	2.61	4.38	0.55	-0.51	0.19
C(8A)	4726	7541	3611	3.60	5.01	3.58	0.65	-0.13	0.37
C(9A)	5178	8297	4128	3.82	4.44	4.48	0.01	-1.38	-0.97
C(10A)	5657	7695	4800	3.83	4.55	4.44	-0.69	-0.16	-0.35
C(11A)	6015	8617	5356	5.49	5.76	4.59	-1.34	-0.40	-0.79
C(12A)	6458	8092	6030	5.42	7.57	4.04	-1.53	-1.09	-0.21
C(13A)	6538	6747	6163	4.67	6.97	5.66	0.70	-0.33	1.58
C(14A)	6188	5799	5607	5.60	6.60	5.95	1.29	0.26	1.27
C(15A)	5741	6261	4927	4.53	5.26	5.14	0.48	-0.12	0.54
C(16A)	2946	10979	1639	6.34	2.70	6.57	2.04	-2.52	1.12
O(2A)	3395	9962	2101	5.54	3.13	6.16	-0.71	-2.08	-0.31
O(4A)	2075	6197	957	5.13	2.75	7.16	-0.21	-2.50	-0.29
O(5A)	2920	4395	1792	5.93	1.95	5.37	-0.13	-1.32	0.15
C(1B)	-311	8519	889	4.49	1.12	4.63	0.44	-0.42	0.66
C(2B)	-821	9410	434	4.60	1.91	4.63	-0.84	0.30	-0.17
C(3B)	-1367	8999	-82	4.83	1.75	4.79	-0.42	-0.76	-0.22
C(4B)	-1456	7515	-211	3.68	4.66	3.24	-0.44	-0.71	-0.20
C(5B)	-944	6544	199	4.04	3.33	4.81	1.22	-0.77	1.51
C(6B)	-409	7027	716	3.75	4.51	4.38	0.72	-1.13	1.05
C(7B)	191	9033	1435	3.91	3.74	3.60	-0.39	-0.97	-0.44
C(8B)	689	8286	1969	3.62	2.99	4.32	-0.37	-0.78	0.13
C(9B)	1151	8959	2503	4.24	3.94	4.73	-0.10	-0.36	-0.33
C(10B)	1661	8312	3112	3.84	4.20	4.01	-0.62	0.06	-0.71
C(11B)	2085	9175	3644	4.94	4.33	6.46	-0.15	-0.54	-0.76
C(12B)	2565	8619	4267	4.29	7.94	5.80	0.26	-1.33	-0.67
C(13B)	2627	7225	4367	6.49	4.85	5.75	0.99	-1.04	0.01
C(14B)	2215	6415	3824	6.92	5.61	6.22	1.25	-0.39	0.36
C(15B)	1741	6923	3209	5.11	3.39	5.52	0.82	-0.89	0.27
C(16B)	-1162	11812	208	5.20	2.04	6.66	0.66	-1.25	1.53
O(2B)	-696	10775	600	5.07	2.76	5.46	-0.11	-1.01	-0.01
O(4B)	-1962	7020	-670	5.31	2.93	5.80	-0.28	-1.65	-0.44
O(5B)	-1054	5200	27	6.84	0.29	8.41	0.21	-1.60	0.02
C(1S)	841	2631	3582	14.56	7.94	7.62	0.85	1.62	0.68
C(2S)	166	2452	3220	7.07	11.40	13.08	-0.44	2.58	-4.25
C(3S)	5	2894	2401	8.38	19.27	13.45	4.73	-3.48	-7.06
C(4S)	539	3379	1974	25.37	11.05	8.89	6.99	0.45	-2.75
C(5S)	1206	3371	2433	19.36	5.42	16.27	-5.40	14.66	-3.67
C(6S)	1335	3049	3203	10.53	9.27	17.45	-3.45	7.95	-4.00
Standard deviations									
O	3	6	3						
C(1-16A)	4	9	4						
C(1-16B)	4	9	4						
C(1-6S)	10	16	12						

constant parameters in the final cycles of refinement. The final R value was 9.5%.*

Fractional coordinates and thermal parameters are listed in Table 1, calculated positions for H atoms are shown in Table 2, and bond lengths and angles are shown in Fig. 1.

Discussion

The two molecules of obtusaquinone in the asymmetric unit are linked by a pair of hydrogen bonds to form the dimer shown in Fig. 1. Molecules A (at x, y, z) and B (at $-x, 1-y, -z$) are nearly related by

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31566 (11 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

a non-crystallographic center (at $x=0.20, y=0.41$ and $z=0.08$) that biases the statistical averages, mentioned earlier, to indicate a hyper-centrosymmetric cell. The two $\text{OH} \cdots \text{O}$ bond lengths, 2.76 and 2.82 Å, are within a normal range. The effects of conjugation between the alternating single and double bonds are quite apparent with the shortening of the 'single' C-C bonds to an average value of 1.46 Å and the lengthening of the 'double' C-C bonds to an average value of 1.35 Å. These values are the same as in other molecules exhibiting conjugation such as 11-*cis*-retinal (Gilardi, Karle & Karle, 1972), and the carotenoid chain (Bart & MacGillavry, 1968), for example.

The methoxy moiety assumes the preferred orientation with the CH_3 carbon coplanar with and directed over the double bond of the ring, rather than the single bond, as demonstrated in methoxycyclohexene (Low-

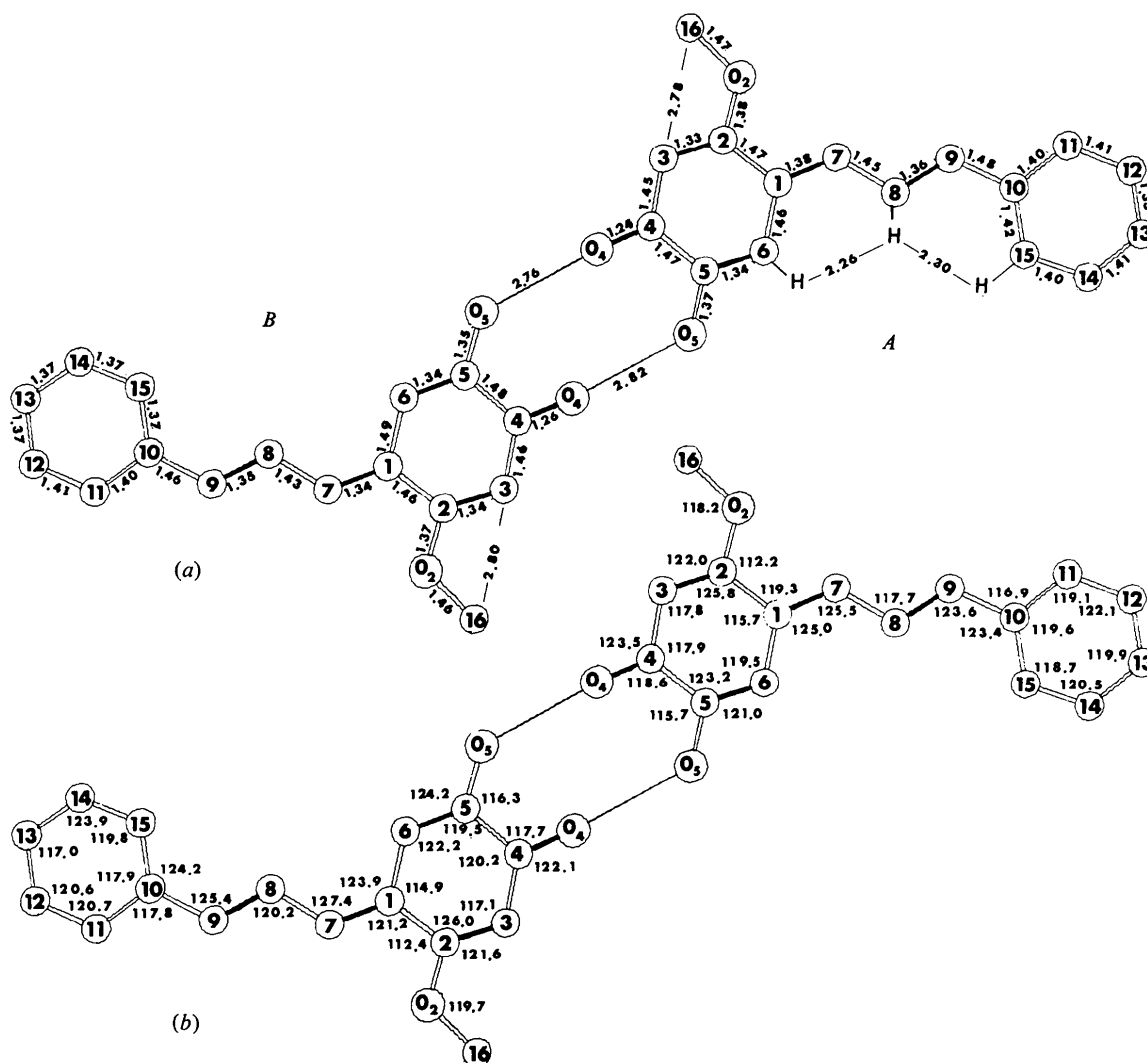


Fig. 1. (a) Bond lengths, hydrogen bonds and some close intramolecular approaches. Double bonds are indicated by the solid lines. The standard deviations for the bonds as determined solely from the least-squares refinement are 0.01 Å. (b) Bond angles. The standard deviations are near 0.7°.

rey, George, D'Antonio & Karle, 1973) and other compounds with similar moieties (see *e.g.* Karle & Karle, 1970). In each case, there is a $\text{CH}_3 \cdots \text{C}_{\text{ring}}$ distance of 2.80 Å or less.

Table 2. Calculated fractional coordinates ($\times 10^3$) for hydrogen atoms

	<i>x</i>	<i>y</i>	<i>z</i>
H(3 <i>A</i>)	239	886	115
H(6 <i>A</i>)	393	555	270
H(7 <i>A</i>)	433	929	300
H(8 <i>A</i>)	471	651	363
H(9 <i>A</i>)	520	932	406
H(11 <i>A</i>)	595	963	527
H(12 <i>A</i>)	672	874	643
H(13 <i>A</i>)	684	641	665
H(14 <i>A</i>)	626	479	570
H(15 <i>A</i>)	549	558	454
H(16 <i>A</i>)	247	1088	177
H(16 <i>A</i>)	294	1082	104
H(16 <i>A</i>)	312	1193	179
H(O5 <i>A</i>)	249	426	139
H(3 <i>B</i>)	-169	969	-36
H(6 <i>B</i>)	-7	634	99
H(7 <i>B</i>)	24	1005	150
H(8 <i>B</i>)	69	726	195
H(9 <i>B</i>)	116	999	250
H(11 <i>B</i>)	205	1020	358
H(12 <i>B</i>)	286	924	464
H(13 <i>B</i>)	296	684	482
H(14 <i>B</i>)	225	539	386
H(15 <i>B</i>)	145	628	283
H(16 <i>B</i>)	-118	1174	-40
H(16 <i>B</i>)	-163	1166	36
H(16 <i>B</i>)	-100	1275	39
H(O5 <i>B</i>)	-148	510	-37
H(1 <i>S</i>)	97	243	418
H(2 <i>S</i>)	-18	203	354
H(3 <i>S</i>)	-48	286	213
H(4 <i>S</i>)	43	369	139
H(5 <i>S</i>)	161	362	216
H(6 <i>S</i>)	181	312	349

The hydrogen atoms on C(6), C(8) and C(15) would approach each other much too closely if the molecule assumed idealized angle values. In order to accommodate these H atoms and maintain atomic radii near their van der Waals value, interior angles C(6)C(1)C(7), C(1)C(7)C(8), C(8)C(9)C(10) and C(9)C(10)C(15) have been increased to an average value of 124.8° while the average value for exterior angles C(7)C(8)C(9) and C(9)C(10)C(11) is 118.1° . The net effect is to spread the distance between C(6) and C(15) so that the separations $\text{H}(6) \cdots \text{H}(8)$ and $\text{H}(8) \cdots \text{H}(15)$ are > 2.2 Å, as shown in Fig. 1. Torsional angles for the four bonds which connect the rings are: C(2)C(1)C(7)C(8) = $+174^\circ$, C(1)C(7)C(8)C(9) = -174° , C(7)C(8)C(9)C(10) = $+175^\circ$, and C(8)C(9)C(10)C(11) = -171° for molecule *A*; and $+175^\circ$, -178° , $+176^\circ$ and -178° , respectively, for molecule *B*.

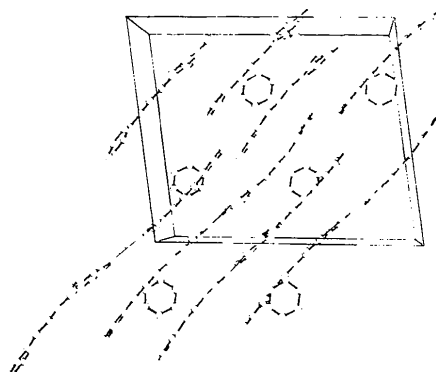


Fig. 2. Packing in the crystal of obtusaquinone. Two independent molecules form dimeric units by a pair of hydrogen bonds spanning the (001) faces. The directions of the axes are: *a* \rightarrow , *c* \swarrow and *b* directed into the page.

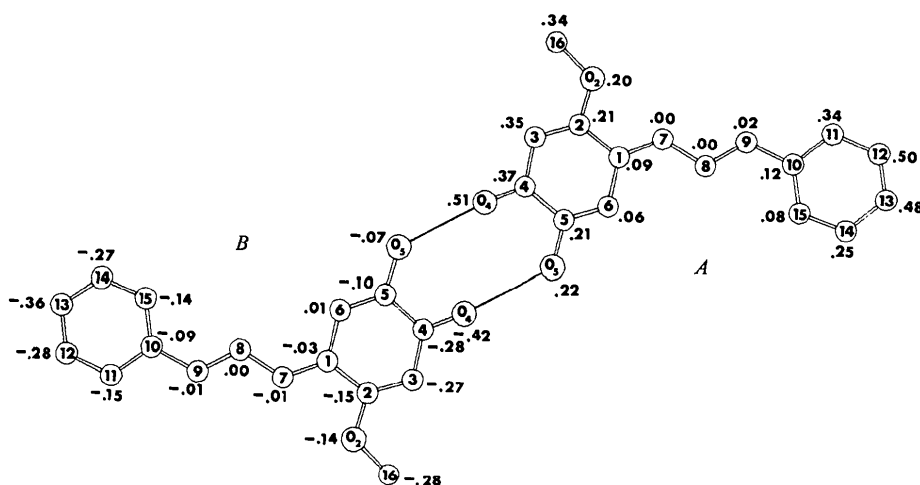
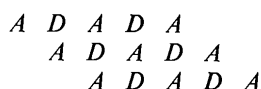


Fig. 3. Deviations from least-squares planes in Å. The equations for the planes are: (molecule *A*) $-14.7255x + 0.5358y + 12.4994z = -1.8130$; (molecule *B*) $-14.2676x - 0.2821y + 12.8908z = -1.4778$. In order to emphasize the bowing, the deviations are measured from planes parallel to the least-squares planes and passing through atoms C(8) in molecules *A* and *B*. The dihedral angle between planes *A* and *B* is 5.2° .

A curious feature of both molecules *A* and *B* is their non-planarity. The *O*-methylobtusaquinone molecule is essentially planar (Palmer, Wong & Jurd, 1973). However, each obtusaquinone molecule is bowed a considerable amount which can be readily seen when the molecules are viewed edge-on as in the packing diagram in Fig. 2. The amount of bowing, up to 0.5 Å in molecule *A* and somewhat less in molecule *B*, is shown in Fig. 3. The tendency of the molecules to exhibit some charge-transfer properties may be a cause of the bowing.

Charge-transfer complexes are deeply colored, ranging from orange to deep purple and black. They are composed of planar molecules with unsaturated groups that act either as donors (*D*) or acceptors (*A*). Usually the molecules are stacked over each other in the sequence (*A*) (*D*) (*A*) (*D*) so that the distance between their planes is of the order of 3.3 to 3.5 Å. A recent extensive study of charge-transfer complexes composed of separate donor and separate acceptor molecules has been made by Tickle & Prout (see *e.g.* Tickle & Prout, 1973) and earlier by Wallwork (1961) and Williams & Wallwork (1967). In some instances, the same molecule acts as both donor and acceptor with different moieties performing the different functions. Such an example is 4-phenylazoazobenzene with donor-acceptor functions alternating in the same molecule, *ADADA*. The stacking pattern in this case is



with a 3.32 Å separation between the planar molecules (Gilardi & Karle, 1972). Another variation is to have auto-complexation where the complexation occurs in

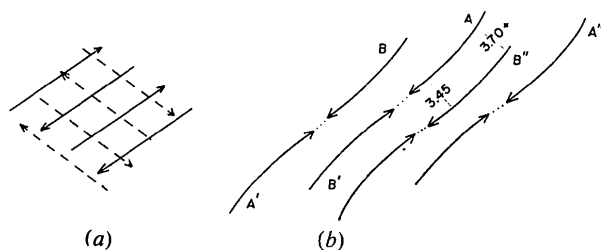


Fig. 4. Schematic representation of packing. (a) *O*-Methylobtusaquinone; head-to-tail array (interaction between quinone and phenyl rings). (b) Obtusaquinone dimers; head-to-head, tail-to-tail array.

the same molecule, \square_4^D , as in 2-(2-pyridylmethylthio)benzoic acid with a separation of 3.24 Å between the planes of the donor and acceptor rings (Karle, Karle & Mitchell, 1969). In each of the above examples, stabilization energy occurred since there is a maximum π - π^* overlap, *i.e.* a double bond of the donor is centered over an aromatic ring of the acceptor (Tickle & Prout, 1973).

In the obtusaquinone cell, Figs. 2 and 4, pairs of molecules consisting of *e.g.* molecule *A* (at x, y, z) and molecule *B* (at $\frac{1}{2}+x, \frac{1}{2}-y, z$) nestle together. The planes passing through the adjacent quinone rings of molecules *A* and *B* have a dihedral angle of 2° and are separated by only 3.45 Å. Distances between individual atoms in the parallel quinone rings range from 3.49 Å for C(3A)···C(4B) to a maximum of 3.54 Å for C(2A)···C(5B). These close approaches are characteristic of charge-transfer compounds although the π - π^* overlap is not ideal. At the other end of the same pair of molecules, the two nearly parallel phenyl rings exhibit a repulsive force between each other. The distances between atoms in the phenyl groups of the two neighboring molecules range from 3.61 to 3.97 Å as compared to 3.5 Å for the quinone moieties. A comparison of the packing in obtusaquinone and its *O*-methyl derivative is shown in Fig. 4. It should be noted that in obtusaquinone the parallel packing is head-to-head, tail-to-tail, while in the *O*-methyl derivative the interaction between the parallel molecules is head-to-tail, *i.e.* an interaction between the quinone ring and phenyl ring.

The crystal packing in obtusaquinone exhibits another interesting feature. The parallel packing of the nearly planar dimers of the molecules creates two channels in the cell parallel to the *a* axis. These channels are near $y=\frac{1}{4}, z=\frac{1}{4}$ and $y=\frac{3}{4}, z=\frac{3}{4}$ and they extend throughout the lattice, Fig. 5. The benzene guest molecule occupies a definite position in the channel, although its thermal parameters are three to four times as large as those for the atoms in the obtusaquinone molecules. The plane of the benzene molecule is inclined near 70° to the planes of the obtusaquinone molecules. At equilibrium the intermolecular approaches between the C atoms of the guest benzene and the C or O atoms of the host obtusaquinone are of the order of 3.7–3.8 Å. The benzene slowly escapes from the lattice upon exposure to air.

In summary, obtusaquinone is an example of a highly conjugated molecule that is significantly bowed

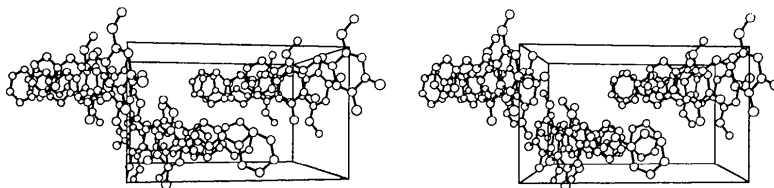


Fig. 5. Channels in the lattice parallel to the *a* axis formed by stacks of four obtusaquinone molecules per cell length. The benzene molecules (not drawn) reside in the channels. The directions of the axes are: *b* ←, *c* ↑ and *a* directed into the page.

rather than being planar, that exists as a dimer, that packs in layers to resemble charge-transfer compounds, and forms a clathrate with benzene as a guest molecule.

References

- BART, J. C. J. & MACGILLAVRY, C. H. (1968). *Acta Cryst.* **B23**, 1569–1587.
- GILARDI, R. D. (1973). *Acta Cryst.* **B29**, 2089–2095.
- GILARDI, R. D. & KARLE, I. L. (1972). *Acta Cryst.* **B28**, 1635–1638.
- GILARDI, R. D., KARLE, I. L. & KARLE, J. (1972). *Acta Cryst.* **B28**, 2605–2612.
- JURD, L., STEVENS, K. & MANNERS, G. (1972a). *Tetrahedron Lett.* pp. 2149–2152.
- JURD, L., STEVENS, K. & MANNERS, G. (1972b). *Phytochemistry*, **11**, 3287–3292.
- KARLE, I. L. & KARLE, J. (1963). *Acta Cryst.* **16**, 969–975.
- KARLE, I. L. & KARLE, J. (1970). *Acta Cryst.* **B26**, 1276–1282.
- KARLE, I. L., KARLE, J. & MITCHELL, D. (1969). *Acta Cryst.* **B25**, 866–871.
- LOWREY, A. H., GEORGE, C. F., D'ANTONIO, P. D. & KARLE, J. (1973). *J. Chem. Phys.* **58**, 2840–2844.
- PALMER, K. J., WONG, R. Y. & JURD, L. (1973). *Acta Cryst.* **B29**, 1509–1514.
- SOUTHWELL, C. R. & BULTMAN, J. D. (1971). *Biotropica*, **3**, 81–107.
- SOUTHWELL, C. R. & BULTMAN, J. D. (1973). Report 7546, Naval Research Laboratory, Washington, D. C., U.S.A.
- TICKLE, I. J. & PROUT, C. K. (1973). *J. Chem. Soc. Perkin II*, pp. 720–734.
- WALLWORK, S. C. (1961). *J. Chem. Soc.* p. 494.
- WILLIAMS, R. M. & WALLWORK, S. C. (1967). *Acta Cryst.* **22**, 899–906.

Acta Cryst. (1976). **B32**, 1968

The Crystal Structures of γ - and β -KNO₃ and the $\alpha \leftarrow \gamma \leftarrow \beta$ Phase Transformations

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On heating KNO₃ at atmospheric pressure, a solid-state phase transformation occurs from α -KNO₃ to β -KNO₃ at $\sim 128^\circ\text{C}$. On cooling from $\sim 200^\circ\text{C}$, β -KNO₃ transforms at $\sim 124^\circ\text{C}$ to γ -KNO₃, which reverts to α -KNO₃ at $\sim 100^\circ\text{C}$. The precise temperature range in which the various phases occur depends on the previous treatment of the sample. X-ray powder diffractometer data have been used to determine the structures of γ - and β -KNO₃, and the hitherto ambiguous situation concerning the NO₃ orientation and disorder has been resolved. For γ -KNO₃ the space group is $R\bar{3}m$ with hexagonal axes $a = 5.487$ (1), $c = 9.156$ (3) Å (91°C), $Z = 3$, while for β -KNO₃ the corresponding data are $R\bar{3}m$, $a = 5.425$ (1), $c = 9.836$ (4) Å (151°C), $Z = 3$. In γ -KNO₃, there are two equivalent types of NO₃ positions, but within each cell the NO₃ groups all belong to one type. With β -KNO₃, each NO₃ is in disorder between the two types of position. Relationships between the structures of the α -, β - and γ -phases are given.

Introduction

At atmospheric pressure, KNO₃ can exist in several different phases depending on the temperature. When heated from room temperature through the transition at $\sim 128^\circ\text{C}$, KNO₃ transforms from an orthorhombic structure (α -KNO₃) to a trigonal structure (β -KNO₃). On cooling the β -phase from $\sim 200^\circ\text{C}$, KNO₃ passes through another trigonal phase (γ -KNO₃) between $\sim 124^\circ\text{C}$ and $\sim 100^\circ\text{C}$ before reverting to the α -phase. γ -KNO₃ exhibits ferroelectric properties (Sawada, Nomura & Fujii, 1958).

The structure of α -KNO₃ has been studied by Edwards (1931) and more recently by Nimmo & Lucas (1972, 1973), the latter using single-crystal neutron diffraction data; the Nimmo & Lucas structure has been confirmed by Holden & Dickinson (1975) with single-crystal X-ray data. The unit cell is orthorhombic with $a = 5.414$ (2), $b = 9.166$ (9), $c = 6.431$ (9) Å (25°C),

$Z = 4$; the space group is $Pm\bar{c}n$ and the structure is of the aragonite type. β -KNO₃ has been investigated by Tahvonen (1947), Shinnaka (1962) and Strømme (1969), and γ -KNO₃ by Barth (1939) and Strømme (1969). In these phases, the NO₃ conformation and orientation is uncertain. Ordered models have been considered for γ -KNO₃, static and dynamic disordered models for β - and γ -KNO₃, and free rotation models for β -KNO₃. The γ -KNO₃ space group has been taken as $R\bar{3}m$, but both $R\bar{3}m$ and $R\bar{3}c$ have been suggested for β -KNO₃. All β - and γ -KNO₃ structural studies have used the X-ray powder diffraction photographic data of Tahvonen (1947) and Barth (1939), respectively. The latter data contained only ten observed reflexions. Shinnaka (1962) also made X-ray diffuse scattering photographic studies.

The aim of the present study was to determine the β - and γ -KNO₃ structures, and to relate the α -, β - and γ -KNO₃ structures.