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# Crystallographic Studies of the Molecular Complexes of *E,E*-1-[*p*-Dimethylaminophenyl]-5-[*o*-Hydroxyphenyl]-penta-1,4-dien-3-one (DHDK) with Chloroform (1:0.4), *m*-Dinitrobenzene (1:1) and *p*-Dimethylaminobenzaldehyde (1:1); the Heilbron Complexes★

*Dedicated to Professor Friedrich Cramer on the occasion of his 60th birthday*

F. H. HERBSTEIN★★, M. KAPON, G. M. REISNER and M. B. RUBIN
*Department of Chemistry, Technion-Israel Institute of Technology, Haifa, Israel 32000*

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**Abstract.** Crystal structures are reported for the molecular complexes of *E,E*-1-[*p*-dimethylaminophenyl]-5-[*o*-hydroxyphenyl]-penta-1,4-dien-3-one (DHDK) with chloroform, *m*-dinitrobenzene and *p*-dimethylaminobenzaldehyde. The three complexes (first reported by I. M. Heilbron and J. S. Buck [1] in 1921) have different structures. In DHDK · 0.4 $CHCl_3$ (triclinic, $a = 12.086(6)$, $b = 10.323(5)$, $c = 8.015(4)$ Å, $\alpha = 94.58(6)$, $\beta = 103.58(6)$, $\gamma = 110.10(6)°$, $Z = 2$, $P\bar{1}$ (assumed)), the host molecules are linked by two hydroxyl – carbonyl hydrogen bonds to form centrosymmetric pairs, with the disordered $CHCl_3$ molecules contained in cavities left between the molecule pairs. The complex is a clathrate. In DHDK · *m*-dinitrobenzene (triclinic, $a = 21.787(9)$, $b = 13.850(5)$, $c = 7.759(4)$ Å, $\alpha = 88.25(5)$, $\beta = 84.70(5)$, $\gamma = 88.86(5)°$, $P\bar{1}$, $Z = 4$) the DHDK molecules are linked in ribbons through head-to-waist hydroxyl – carbonyl hydrogen bonds. The guest molecules are contained in sinuous channels left between the DHDK ribbons; the host and guest molecules are approximately coplanar. Successive planes are mutually shifted so that the guest molecules are enclosed above and below by host molecules. This is a new structural type, with features resembling those of channel inclusion complexes. In DHDK · *p*-dimethylaminobenzaldehyde (monoclinic, $a = 22.331(9)$, $b = 12.238(5)$, $c = 8.904(4)$ Å, $\beta = 92.99(5)°$, $Z = 4$, $P2_1/n$) the host molecules are arranged so as to leave channels of approximately rectangular cross-sections in which the guest molecules are accommodated. Additional stabilization is achieved by hydrogen bonding between host hydroxyl and guest carbonyl groups. This is a channel-inclusion complex. In the chloroform and *p*-dimethylaminobenzaldehyde complexes the host molecule has the *s-trans, trans* conformation but in the *m*-dinitrobenzene complex its conformation is *s-cis, trans*.

**Key words:** Inclusion, clathrate, clathrand, host/guest, X-ray analysis, Heilbron complexes.

**Supplementary Data** relating to this article are deposited with the British Library as Supplementary Publication No. SUP 90076 (13 pages). To obtain copies, see page ii of this issue.

★ 'Molecular Compounds and Complexes', Part XIV. For Part XIII, see [25].
★★ Author for correspondence.

## 1. Introduction

Heilbron and Buck [1] reported the preparation of some 15 rather stable complexes of 1-[*p*-dimethylaminophenyl]-5-[*o*-hydroxyphenyl]-penta-1,4-dien-3-one (DHDK★) with such different molecules as chloroform, phenanthrene (an electron donor) and 2,4,6-trinitrotoluene (TNT, an electron acceptor). The colours of the complexes were reported to vary from yellow to black, suggesting a variety of types of interaction between the components. The authors commented that "the ketone is very difficult to obtain in the free state as it tenaciously retains traces of solvent"; they also showed that the *o*-methoxyphenyl analogue of DHDK formed complexes only with electron acceptors such as *m*-dinitrobenzene and 1,3,5-trinitrobenzene. No further investigation appears to have been made of this intriguing system in the 60-odd years that have elapsed since the original report. We have been able to prepare many but not all of the complexes reported by Heilbron and Buck, and have carried out X-ray crystal structure analyses of three complexes.

## 2. Experimental

### 2.1. PREPARATION OF THE COMPLEXES

The original procedure of Heilbron and Buck [1] for the preparation of the *p*-dimethylaminobenzaldehyde (PDMB) complex by reaction of salicylidene acetone and PDMB could not be reproduced until an additional operation, partial neutralization of the alkaline solution, was introduced.

A mixture of salicylidene acetone (1.6 g) and PDMB (2.2 g) in 95% ethanol (15 ml) was treated with 10% sodium hydroxide solution (8 ml). After 48 h in the dark at room temperature, the deep red solution was treated with excess dry ice. The addition of water (33 ml) caused the separation of a dark tar. The aqueous phase was decanted, the tar washed several times with water and then dried *in vacuo*. Trituration with absolute ethanol led to crystallization; large, dark red crystals of the DHDK · PDMB complex, m.p. 138–142°, were obtained. Heating this complex with benzene led to replacement of PDMB by benzene, giving DHDK · $C_6H_6$. Other solvents (or solutions) behaved similarly, giving the appropriate complexes.

The pure ketone was obtained, in polycrystalline form, by recrystallization from ethylacetoacetate. Single crystals could not be prepared. A sample of DHDK dissolved in ethyl acetate and precipitated by addition of *n*-heptane was found to be non-crystalline.

### 2.2. PRELIMINARY X-RAY DIFFRACTION STUDIES OF THE COMPLEXES

A preliminary classification of the complexes was based on results from single crystal and powder diffraction studies. All unit cell dimensions derived from single crystal studies (Table I) were reduced [2, 3] using the programme TRACER [4]. The following conclusions could be drawn:

(1) DHDK · 0.4 $CHCl_3$ and DHDK · 0.5 $C_2H_5OH$ are isomorphous and DHDK · $CH_3COOH$ is closely related structurally (Table I, single crystal studies). The structure of DHDK · 0.4 $CHCl_3$ is described below. We call these Group I structures.

★ Heilbron and Buck [1] used the name 4′-dimethylamino-2-hydroxydistyryl ketone and our acronym (DHDK) is based on this name.

Table I. Single crystal data for some molecular complexes of DHDK. All cell dimensions were measured on a four-circle diffractometer. DHDK = $C_{19}H_{19}O_2N$; PDMB = $C_9H_{11}ON$

| Parameter | DHDK · 0.4 $CHCl_3$ | DHDK · 0.5 $C_2H_5OH$ | DHDK · $CH_3COOH$ | DHDK · $CH_3OH$ | DHDK · $m$-$C_6H_4(NO_2)_2$ | DHDK · PDMB |
|---|---|---|---|---|---|---|
| $a$ (Å) | 12.086(6) | 12.039(8) | 12.379(8) | 13.931(8) | 21.787(9) | 22.383(9) |
| $b$ | 10.323(5) | 10.252(7) | 10.194(7) | 12.541(7) | 13.850(6) | 12.272(5) |
| $c$ | 8.015(4) | 7.879(4) | 7.819(4) | 10.570(6) | 7.759(4) | 8.917(4) |
| $\alpha$ (deg) | 94.58(6) | 93.64(8) | 94.78(8) | 68.28(7) | 88.25(5) | – |
| $\beta$ | 103.58(6) | 104.64(8) | 96.70(8) | 73.33(7) | 84.70(5) | 92.99(5) |
| $\gamma$ | 110.10(6) | 110.58(8) | 109.82(8) | 73.94(7) | 88.86(5) | – |
| $D_m$ (g × $cm^{-3}$) | 1.27 | 1.21 | 1.27 | 1.32 | 1.31 | 1.21 |
| $D_c$ | 1.27 | 1.21 | 1.28 | 1.34 | 1.31 | 1.20 |
| $Z$ | 2 | 2 | 2 | 4 | 4 | 4 |
| Space group | $P\bar{1}$ [a] | $P\bar{1}$ | $P\bar{1}$ [a] | $P\bar{1}$ [a] | $P\bar{1}$ [a] | $P2_1/n$ |
| Vol. of cell (Å$^3$) | 898.60 | 868.29 | 913.88 | 1613.00 | 2329.9 | 2446.02 |

[a] Could also be $P1$.

*Notes:*

1. The unit cells given for DHDK · 0.4 $CHCl_3$ and DHDK · 0.5 $C_2H_5OH$ are both the Dirichlet and Delaunay reduced triclinic cells (see [2, 3] for discussion of definition of triclinic cells).
2. The unit cells given for DHDK · $CH_3COOH$ and DHDK · $m$-dinitrobenzene are both Dirichlet (but not Delaunay) reduced cells.
3. The compositions are calculated from the measured densities.
4. Mo $K\alpha$ radiation was used, except for DHDK · $m$-dinitrobenzene where Cu $K\alpha$ was used (Mo $K\alpha$ = 0.7107 Å, Cu $K\alpha$ = 1.5418 Å).

(2) DHDK · 2(TNT) and DHDK · 2(TNB) give similar powder patterns while oscillation photographs of apparent single crystals give fibre patterns with a needle-axis repeat of ~7 Å. The structures appear to be closely related but could not be determined because of the lack of true single crystals.

(3) DHDK · *m*-dinitrobenzene and DHDK · anisaldehyde (4-methoxybenzaldehyde) give similar powder photographs. The structure of the former is described below.

(4) A complex was obtained from a methanol solution of DHDK. This complex has distinct cell dimensions (Table I) and was formulated as DHDK · $CH_3OH$ on the basis of the measured density. A chemical analysis was not made because of a lack of material but mass spectrometry confirmed that the sample contained methanol. Single crystals obtained from methanol solutions of DHDK/phenanthrene and DHDK/fluorene gave the same diffraction patterns as DHDK · $CH_3OH$. Thus, we did not obtain the complexes of DHDK with phenanthrene and fluorene reported by Heilbron and Buck (and identified by them only on the basis of C, H analyses).

(5) The powder pattern of pure DHDK (obtained, following Heilbron and Buck, by precipitation from ethylacetoacetate or by heating the ethanol complex) was the same as those from *powdered* samples of complexes of DHDK with $CHCl_3$, $C_2H_5OH$ and $CH_3OH$, and purported complexes with phenol, carbazole, phenanthrene and fluorene. We infer, as above, that complexes were not formed with the non-volatile guests, and that the volatile guests evaporated during the process of preparing powdered samples from the solid products of crystallization.

(6) Complexes prepared with $CHCl_3$ (blue form), $CH_2Cl_2$, aniline and hydroxylamine all gave different powder patterns, which were also different from those noted above. Thus, we infer that complexes were formed. Single crystals of these complexes were not obtained.

### 2.3. DETERMINATION OF CRYSTAL STRUCTURES

Three crystal structures were determined. Similar methods were used and details are summarized in Table II. Preliminary diffraction photographs were taken of all the crystals

Table II. Summary of experimental conditions, methods and results of the crystal structure determinations. No absorption corrections were made

| Parameter | DHDK.0.4 $CHCl_3$ | DHDK · *m*-$C_6H_4(NO_2)_2$ | DHDK · PDMB |
|---|---|---|---|
| Speed (°$\omega$/s) | 0.050 | 0.050 | 0.050 |
| Slit width (°$\omega$) | 1.40 | 1.20 + 0.15 tan $\theta$ | 1.40 |
| Background (total, s) | 28 | 24 | 28 |
| Method of intensity measurement | $\omega/2\theta$ | $\omega/2\theta$ | $\omega/2\theta$ |
| Theta limits (deg) | $2 \leq \theta \leq 25$ | $3 \leq \theta \leq 65$ | $1.5 \leq \theta \leq 25$ |
| $\mu$ ($cm^{-1}$) | 2.56 (Mo$K\alpha$) | 8.00 (Cu$K\alpha$) | 0.84 (Mo$K\alpha$) |
| No. of reflections used in the final refinement stage | 1535 | 6033 | 2641 |
| Weighting scheme $w(F) = a/[\sigma^2(F_{obs}) + bF^2]$ | unit | $a$ = 1.77<br>$b$ = 0.0007 | 1.85<br>0.001 |
| $R_F$ (%) | 15.5 | 7.1 | 10.3 |
| $R_W$ (%) | – | 7.6 | 9.2 |
| Conditions on reflections used in final refinement stage ($F_{obs} \geq k\sigma(F_{obs})$) | $k$ = 5 | $k$ = 1.5 | $k$ = 1.5 |
| No. of reflections suppressed | 1506 | 1667 | 1373 |
| No. of parameters refined | 186 | 275 1st bloc<br>249 2nd bloc | 427 |

used in order to establish quality and absence of twinning; cell dimension and intensity measurements were then made, at room temperature, using a Philips PW 1100 four-circle diffractometer. All crystals were found to be stable over the period of intensity measurements. Structure factors and anisotropic temperature factors have been deposited (see p. 233), except for DHDK · 0.4 $CHCl_3$ (see below).

Specific points of interest will be noted for the three complexes.

(i) DHDK · 0.4$CHCl_3$: Although parallel sets of intensity measurements were made on the isomorphous $CHCl_3$ and $C_2H_5OH$ complexes, only the $CHCl_3$ complex has been studied in detail because it gave a far better set of intensity measurements. Considerable difficulty was experienced in the solution and refinement of the structure. The space group was initially assumed to be $P\bar{1}$. A Patterson synthesis was calculated but could not be interpreted; specifically, the Cl...Cl vectors could not be identified. Direct methods [5] were then used; superimposed sets of molecular images were found which were resolved by suitable mutual shifts [6]. This trial structure, incorporating only the DHDK molecules, refined to $R \sim 20\%$. A difference synthesis showed residual density around $0, \frac{1}{2}, 0$ and the $CHCl_3$ molecule was introduced into this region. As not enough material was available for chemical analysis, the crystal composition was inferred from careful density measurements; for the $CHCl_3$ complex, the composition DHDK · 0.4 $CHCl_3$ gives the best fit to the measured density while for the $C_2H_5OH$ complex the sensitivity is less and so the nominal composition DHDK · 0.5 $C_2H_5OH$ is given. In space group $P\bar{1}$ the $CHCl_3$ molecule must be orientationally disordered to give a centrosymmetric electron density distribution about $0, \frac{1}{2}, 0$; further, about

Table III. DHDK · 0.4 $CHCl_3$ – atomic coordinates ($\times 10^4$). Parameters of hydrogens are not given, although included in the refinement. The parameters of the Cl atoms of the disordered $CHCl_3$ molecules refer to the principal orientation only. The values of $U_{eq}$ ($\times 10^3$) are of indicative value only ($U_{eq} = \frac{1}{3}$ tr of the orthogonalized tensor)

| Atom | $x$ | $y$ | $z$ | $U_{eq}$ (Å$^2$) |
|---|---|---|---|---|
| C(1) | 7912(11) | 883(12) | 5183(15) | 70 |
| C(2) | 8880(12) | 1857(13) | 4742(17) | 75 |
| C(3) | 8844(11) | 3122(13) | 4359(19) | 88 |
| C(4) | 7805(16) | 3374(15) | 4236(23) | 119 |
| C(5) | 6788(13) | 2405(16) | 4484(22) | 110 |
| C(6) | 6850(12) | 1151(15) | 4969(21) | 98 |
| C(7) | 8037(10) | − 432(12) | 5653(15) | 63 |
| C(8) | 7151(10) | − 1514(13) | 5895(15) | 68 |
| C(9) | 7362(10) | − 2709(13) | 6422(15) | 55 |
| C(10) | 6323(10) | − 3746(13) | 6836(16) | 69 |
| C(11) | 6270(10) | − 4905(14) | 7323(15) | 64 |
| C(12) | 5340(10) | − 5955(12) | 7880(14) | 62 |
| C(13) | 5509(10) | − 7131(14) | 8382(20) | 99 |
| C(14) | 4632(11) | − 8094(12) | 8896(18) | 81 |
| C(15) | 3473(11) | − 8072(12) | 8883(14) | 61 |
| C(16) | 3311(10) | − 6885(12) | 8339(15) | 48 |
| C(17) | 4238(11) | − 5832(11) | 7880(14) | 61 |
| N(1) | 2628(8) | − 9053(10) | 9323(13) | 74 |
| O(1) | 9944(7) | 1620(8) | 4976(12) | 100 |
| O(2) | 8264(8) | − 3021(8) | 6418(12) | 83 |
| | | | | $U_{iso}$ (Å$^2$) |
| Cl(1) | 8677(9) | 4701(11) | 798(13) | 143 |
| Cl(2) | 10941(15) | 6570(14) | 796(16) | 168 |
| Cl(3) | 10200(15) | 3814(14) | − 1019(19) | 189 |

Table IV. DHDK: *m*-dinitrobenzene – atomic coordinates ( $\times 10^4$ for non-hydrogen atoms; $\times 10^3$ for hydrogens), equivalent isotropic temperature factors for non-hydrogen atoms and isotropic temperature factors for hydrogen atoms (both $\times 10^3$)

| | Atom | *x* | *y* | *z* | $U_{eq}$ (Å$^2$) |
|---|---|---|---|---|---|
| DHDK-A | C(1A) | −1311(1) | 1578(2) | 122(3) | 53 |
| | C(2A) | −1688(1) | 821(2) | 839(4) | 55 |
| | C(3A) | −1525(2) | −129(3) | 564(5) | 66 |
| | C(4A) | −989(2) | −359(3) | −402(5) | 75 |
| | C(5A) | −611(2) | 358(3) | −1131(4) | 70 |
| | C(6A) | −771(2) | 1307(3) | −859(4) | 63 |
| | O(1A) | −2216(1) | 1073(2) | 1838(3) | 69 |
| | C(7A) | −1481(2) | 2574(2) | 421(4) | 55 |
| | C(8A) | −1181(1) | 3349(2) | −191(4) | 61 |
| | C(9A) | −1382(1) | 4328(2) | 219(4) | 61 |
| | O(2A) | −1860(1) | 4467(1) | 1189(3) | 83 |
| | C(10A) | −1033(2) | 5160(2) | −500(4) | 63 |
| | C(11A) | −528(2) | 5128(2) | −1610(4) | 59 |
| | C(12A) | −167(1) | 5914(2) | −2380(4) | 57 |
| | C(13A) | −305(2) | 6891(2) | −2099(4) | 60 |
| | C(14A) | 54(1) | 7602(2) | −2823(4) | 61 |
| | C(15A) | 595(1) | 7412(2) | −3909(4) | 59 |
| | C(16A) | 731(2) | 6430(2) | −4221(4) | 66 |
| | C(17A) | 360(2) | 5721(3) | −3482(4) | 67 |
| | N(1A) | 968(1) | 8120(2) | −4584(4) | 77 |
| | C(18A) | 797(3) | 9120(3) | −4379(7) | 84 |
| | C(19A) | 1574(2) | 7915(4) | −5439(7) | 89 |
| *m*-dinitro- | C(20A) | 2035(1) | 3579(2) | 3266(4) | 66 |
| benzene A | C(21A) | 1585(2) | 3476(2) | 4613(4) | 70 |
| | C(22A) | 1372(2) | 2564(3) | 4998(4) | 75 |
| | C(23A) | 1613(2) | 1775(3) | 4101(6) | 95 |
| | C(24A) | 2062(2) | 1909(3) | 2764(6) | 100 |
| | C(25A) | 2272(2) | 2811(3) | 2318(6) | 83 |
| | N(2A) | 2276(1) | 4557(2) | 2811(4) | 80 |
| | O(3A) | 2027(1) | 5243(2) | 3534(4) | 104 |
| | O(4A) | 2721(1) | 4612(2) | 1732(4) | 110 |
| | N(3A) | 878(2) | 2441(3) | 6421(5) | 106 |
| | O(5A) | 683(2) | 3150(3) | 7197(4) | 147 |
| | O(6A) | 669(2) | 1628(3) | 6628(4) | 143 |
| DHDK-B | C(1B) | 6696(1) | −3441(2) | 4100(3) | 55 |
| | C(2B) | 7065(1) | −4182(2) | 3337(3) | 55 |
| | C(3B) | 6915(2) | −5136(2) | 3666(4) | 68 |
| | C(4B) | 6403(2) | −5377(3) | 4745(5) | 86 |
| | C(5B) | 6026(2) | −4656(2) | 5493(5) | 83 |
| | C(6B) | 6178(2) | −3712(2) | 5171(4) | 69 |
| | O(1B) | 7572(1) | −3922(1) | 2267(3) | 69 |
| | C(7B) | 6867(1) | −2433(2) | 3794(4) | 58 |
| | C(8B) | 6558(2) | −1667(2) | 4366(4) | 67 |
| | C(9B) | 6780(2) | 682(2) | 3991(4) | 68 |
| | O(2B) | 7276(1) | −559(1) | 3111(3) | 96 |
| | C(10B) | 6427(2) | 148(2) | 4655(4) | 66 |
| | C(11B) | 5907(2) | 106(2) | 5698(4) | 62 |
| | C(12B) | 5539(1) | 888(2) | 6471(4) | 57 |
| | C(13B) | 5659(1) | 1876(2) | 6186(4) | 63 |

Table IV (continued)

| | Atom | $x$ | $y$ | $z$ | $U_{eq}$ (Å$^2$) |
|---|---|---|---|---|---|
| | C(14B) | 5298(1) | 2576(2) | 6988(4) | 65 |
| | C(15B) | 4786(1) | 2344(2) | 8161(4) | 60 |
| | C(16B) | 4665(2) | 1365(2) | 8441(4) | 65 |
| | C(17B) | 5027(1) | 672(2) | 7609(4) | 68 |
| | N(1B) | 4433(1) | 3035(2) | 9004(3) | 74 |
| | C(18B) | 4568(3) | 4052(3) | 8768(7) | 96 |
| | C(19B) | 3896(2) | 2781(3) | 10134(6) | 85 |
| *m*-dinitro- | C(20B) | 4039(1) | −2472(2) | −973(4) | 62 |
| benzene B | C(21B) | 3862(1) | −1554(2) | −475(4) | 61 |
| | C(22B) | 3328(1) | −1462(2) | 572(4) | 65 |
| | C(23B) | 2968(2) | −2233(3) | 1101(6) | 87 |
| | C(24B) | 3160(2) | −3124(3) | 601(6) | 103 |
| | C(25B) | 3699(2) | −3261(3) | −465(5) | 85 |
| | N(2B) | 4625(1) | −2599(2) | −2068(3) | 73 |
| | O(3B) | 4930(1) | −1897(2) | −2490(3) | 86 |
| | O(4B) | 4770(1) | −3421(2) | −2508(3) | 101 |
| | N(3B) | 3119(1) | −488(2) | 1123(4) | 79 |
| | O(5B) | 3411(1) | 201(2) | 558(4) | 106 |
| | O(6B) | 2666(1) | −429(2) | 2171(4) | 107 |
| | | | | | $U_{iso}$ (Å$^2$) |
| DHDK-A | H(1A) | −234(2) | 45(3) | 226(5) | 130 |
| | H(3A) | −178(1) | −55(2) | 98(4) | 84 |
| | H(4A) | −89(1) | −97(2) | −67(4) | 71 |
| | H(5A) | −27(1) | 23(2) | −162(4) | 74 |
| | H(6A) | −49(1) | 172(2) | −125(4) | 74 |
| | H(7A) | −185(1) | 266(2) | 121(4) | 68 |
| | H(8A) | −80(2) | 317(2) | −97(5) | 112 |
| | H(10A) | −120(1) | 577(2) | −13(4) | 66 |
| | H(11A) | −39(1) | 448(2) | −187(3) | 61 |
| | H(13A) | −63(1) | 706(2) | −138(4) | 63 |
| | H(14A) | 0(1) | 819(2) | −259(3) | 65 |
| | H(16A) | 105(2) | 628(2) | −488(4) | 97 |
| | H(17A) | 48(1) | 513(2) | −368(4) | 62 |
| | H(181A) | 78(2) | 931(3) | −316(5) | 99 |
| | H(182A) | 41(2) | 932(3) | −447(7) | 134 |
| | H(183A) | 106(2) | 951(3) | −501(5) | 118 |
| | H(191A) | 181(2) | 744(3) | −475(6) | 114 |
| | H(192A) | 160(2) | 754(3) | −623(6) | 113 |
| | H(193A) | 175(3) | 845(4) | −555(8) | 232 |
| *m*-dinitro- | H(21A) | 139(2) | 401(2) | 528(4) | 108 |
| benzene A | H(23A) | 147(2) | 113(3) | 451(5) | 118 |
| | H(24A) | 226(2) | 134(3) | 204(5) | 127 |
| | H(25A) | 256(1) | 291(2) | 151(4) | 78 |
| DHDK-B | H(1B) | 780(1) | 546(2) | 193(4) | 107 |
| | H(3B) | 718(1) | −560(2) | 322(4) | 88 |
| | H(4B) | 631(2) | −594(3) | 496(5) | 103 |
| | H(5B) | 564(2) | −477(2) | 621(4) | 104 |
| | H(6B) | 593(1) | −325(2) | 559(4) | 59 |
| | H(7B) | 725(1) | 766(2) | 303(4) | 77 |
| | H(8B) | 623(2) | 822(2) | 510(4) | 97 |
| | H(10B) | 661(1) | 1069(2) | 436(4) | 74 |
| | H(11B) | 578(2) | 949(2) | 605(4) | 108 |
| | H(13B) | 602(1) | 210(2) | 545(4) | 84 |

Table IV (continued)

| | Atom | $x$ | $y$ | $z$ | $U_{eq}$ (Å$^2$) |
|---|---|---|---|---|---|
| | H(14B) | 539(1) | 322(2) | 680(4) | 76 |
| | H(16B) | 431(2) | 126(2) | 920(5) | 115 |
| | H(17B) | 498(1) | 4(2) | 776(4) | 82 |
| | H(181B) | 497(2) | 412(3) | 888(5) | 110 |
| | H(182B) | 452(2) | 428(3) | 747(5) | 116 |
| | H(183B) | 429(3) | 430(4) | 924(7) | 201 |
| | H(191B) | 366(2) | 323(3) | 1038(6) | 130 |
| | H(192B) | 401(2) | 241(2) | 1120(5) | 121 |
| | H(193B) | 362(2) | 238(3) | 951(5) | 143 |
| *m*-dinitro- | H(21B) | 409(1) | −102(2) | −91(3) | 58 |
| benzene B | H(23B) | 260(2) | −205(2) | 195(5) | 124 |
| | H(24B) | 294(1) | −363(2) | 93(3) | 106 |
| | H(25B) | 385(1) | −386(2) | −94(4) | 100 |

20% of these cavities are vacant. The difference synthesis suggested a major and some minor orientations for the $CHCl_3$ molecule but these could not be defined in detail, despite a series of long and tedious refinements using the various options of SHELX-77 [7] which converged at $R = 15.5\%$. An attempt was then made to refine in space group $P1$ which permits the $CHCl_3$ molecule to be orientationally ordered; the $R$-factor was reduced to 13.1%. It is not clear whether removal of the centre of symmetry constitutes a physically-real improvement; at this level of refinement and with the problem caused by disorder, it does not seem justified to apply the criteria of Hamilton [8] to decide between the space groups. Thus, the results will be described in terms of space group $P\bar{1}$ without attempting to define the position of the $CHCl_3$ molecule in any detail. The atomic parameters are given in Table III. The dimensions of the DHDK molecule and its temperature factors are reasonably satisfactory but anisotropic temperature factors and structure factor tables have not been deposited as this does not seem to be warranted by the level of refinement achieved.

(ii) DHDK · *m*-dinitrobenzene and DHDK · PDMB: The two structures were solved by direct methods [5] and refined by least-squares techniques [7]. Molecular models of the relevant components were introduced to obtain an improved scaling of the $E$-values. Solution of the DHDK · *m*-dinitrobenzene structure required a modification of the MULTAN programme to accept 800 $E$-values, as there are 68 non-hydrogen atoms (two formula units) in the asymmetric unit. All the hydrogen atoms were found from the corresponding difference-Fourier syntheses. Final atomic parameters of the compounds are in Tables IV and V respectively.

## 3. Crystal Structures

### 3.1. CRYSTAL STRUCTURE OF DHDK · 0.4 $CHCl_3$, A REPRESENTATIVE OF THE GROUP I STRUCTURES

The most important feature of the crystal structure of DHDK · 0.4 $CHCl_3$ is the formation of centrosymmetric pairs of DHDK molecules by hydrogen bonding between carbonyl

Table V. DHDK · PDMB – atomic parameters ( $\times 10^4$ for non-hydrogen atoms and $\times 10^3$ for hydrogens)

| | Atom | $x$ | $y$ | $z$ | $U_{eq}$ (Å$^2$) |
|---|---|---|---|---|---|
| DHDK | C(1) | 2276(3) | −1610(5) | 7110(7) | 549 |
| | C(2) | 2659(3) | −2269(5) | 8010(8) | 641 |
| | C(3) | 3171(3) | −2730(6) | 7439(9) | 774 |
| | C(4) | 3304(4) | −2529(7) | 5972(10) | 917 |
| | C(5) | 2940(4) | −1851(7) | 5070(9) | 885 |
| | C(6) | 2423(3) | −1424(6) | 5633(8) | 724 |
| | C(7) | 1748(3) | −1127(5) | 7734(7) | 538 |
| | C(8) | 1328(3) | −520(5) | 7048(7) | 538 |
| | C(9) | 828(3) | −75(5) | 7845(7) | 552 |
| | C(10) | 391(3) | 614(5) | 7003(7) | 555 |
| | C(11) | −98(3) | 1008(5) | 7607(7) | 550 |
| | C(12) | −546(3) | 1742(4) | 6984(7) | 506 |
| | C(13) | −1026(3) | 2036(5) | 7856(7) | 565 |
| | C(14) | −1452(3) | 2798(5) | 7398(8) | 622 |
| | C(15) | −1413(3) | 3317(5) | 5995(8) | 582 |
| | C(16) | −952(3) | 3003(5) | 5092(7) | 575 |
| | C(17) | −528(3) | 2244(5) | 5577(7) | 528 |
| | C(18) | −1841(4) | 4539(6) | 4049(9) | 921 |
| | C(19) | −2260(4) | 4507(7) | 6489(12) | 1115 |
| | N(1) | −1810(3) | 4108(5) | 5560(7) | 817 |
| | O(1) | 2526(2) | −2443(4) | 9454(6) | 872 |
| | O(2) | 772(2) | −256(4) | 9193(5) | 714 |
| | | | | | $U_{iso}$ (Å$^2$) |
| | HC(3) | 344(2) | −318(4) | 806(5) | 90 |
| | HC(4) | 368(2) | −281(4) | 554(5) | 121 |
| | HC(5) | 293(2) | −182(4) | 391(6) | 128 |
| | HC(6) | 213(2) | −96(4) | 501(5) | 82 |
| | HC(7) | 171(2) | −125(4) | 871(5) | 59 |
| | HC(8) | 132(2) | −35(4) | 602(5) | 84 |
| | HC(10) | 49(2) | 77(3) | 609(5) | 62 |
| | HC(11) | −15(2) | 80(3) | 858(5) | 44 |
| | HC(13) | −104(2) | 174(4) | 881(5) | 108 |
| | HC(14) | −180(2) | 297(3) | 808(4) | 60 |
| | HC(16) | −92(2) | 331(4) | 411(5) | 68 |
| | HC(17) | −22(2) | 210(3) | 496(5) | 55 |
| | HC(18)A | −174(2) | 403(3) | 333(5) | 87 |
| | HC(18)B | −216(2) | 503(4) | 403(5) | 138 |
| | HC(18)C | −147(2) | 490(4) | 386(5) | 111 |
| | HC(19)A | −255(2) | 390(4) | 681(6) | 106 |
| | HC(19)B | −248(2) | 510(4) | 621(5) | 105 |
| | HC(19)C | −201(2) | 483(4) | 746(4) | 129 |
| | HO(1) | 280(2) | −310(4) | 986(4) | 88 |
| PDMB | C(20) | 5858(3) | 2839(6) | 7739(6) | 655 |
| | C(21) | 5366(3) | 2977(5) | 6706(6) | 712 |
| | C(22) | 4962(3) | 2176(5) | 6378(6) | 714 |
| | C(23) | 5029(3) | 1149(5) | 7074(6) | 712 |
| | C(24) | 5534(3) | 990(5) | 8092(6) | 759 |
| | C(25) | 5918(3) | 1813(5) | 8409(6) | 717 |
| | C(26) | 6257(3) | 3743(5) | 8041(7) | 788 |
| | C(27) | 4683(3) | −745(5) | 7413(8) | 1157 |
| | C(28) | 4122(3) | 492(5) | 5695(8) | 1068 |

Table V (continued)

| Atom | $x$ | $y$ | $z$ | $U_{eq}$ (Å$^2$) |
|---|---|---|---|---|
| N(2) | 4620(2) | 339(4) | 6765(6) | 838 |
| O(3) | 6693(2) | 3752(4) | 8944(5) | 916 |
| | | | | $U_{iso}$ (Å) |
| HC(21) | 532(2) | 372(4) | 624(5) | 88 |
| HC(22) | 460(2) | 238(4) | 578(5) | 101 |
| HC(24) | 556(2) | 33(4) | 857(5) | 90 |
| HC(25) | 626(2) | 170(4) | 907(5) | 98 |
| HC(26) | 618(2) | 440(4) | 735(5) | 90 |
| HC(27)A | 496(2) | −95(4) | 741(6) | 114 |
| HC(27)B | 467(2) | −78(4) | 838(6) | 107 |
| HC(27)C | 437(2) | −120(4) | 709(5) | 121 |
| HC(28)A | 390(2) | 111(4) | 600(5) | 91 |
| HC(28)B | 389(2) | −6(5) | 572(6) | 102 |
| HC(28)C | 577(2) | −64(4) | 1539(5) | 126 |

and hydroxyl groups. The approximately planar molecular pairs are arranged in sheets parallel to (112). In Figure 1, two successive such sheets are shown related by the centre of symmetry at $0, \frac{1}{2}, 0$, leaving a cavity centered at this position. The upper and lower ends of this cavity are closed off by *o*-hydroxyphenyl rings of two equivalent DHDK molecules separated by translation along [001]. The DHDK molecule has the *s-trans, trans* conformation. This nomenclature is based on that used [9] for the conformers of dibenzylidene acetone (1,5-diphenyl-1,4-pentadien-3-one) of [**I** to **III**]. We use 'configuration' to describe the arrangements of substituents about a formal double bond and 'conformation' for that about a formal single bond. Isomerism about a double bond is designated *cis, trans* (or *Z, E*) and about a single bond *s-cis* or *s-trans*. *E, E*-1-[*p*-dimethylaminophenyl]-5-[*o*-hydroxy-

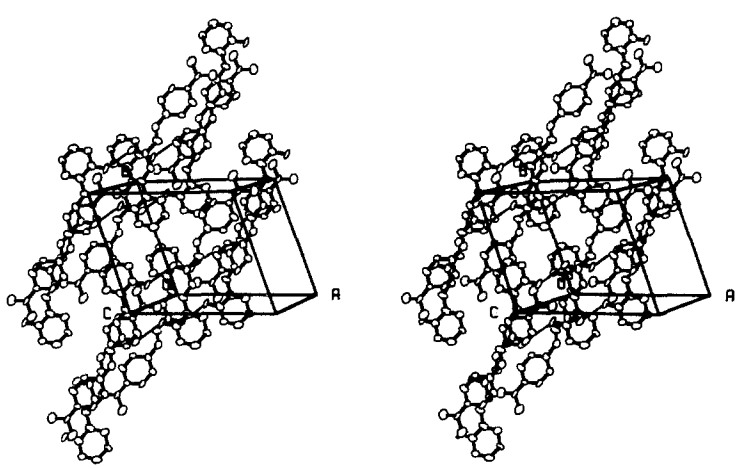
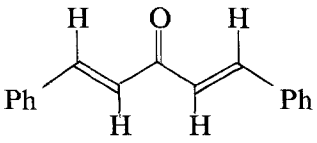
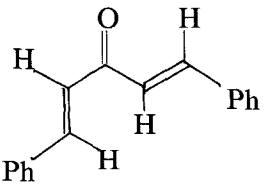


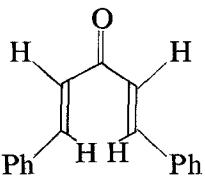

Fig. 1. DHDK · 0.4 $CHCl_3$ – stereodiagram of the crystal structure. The thermal motion ellipsoids represent 40% probability distributions.




*s-trans, trans* **(I)**



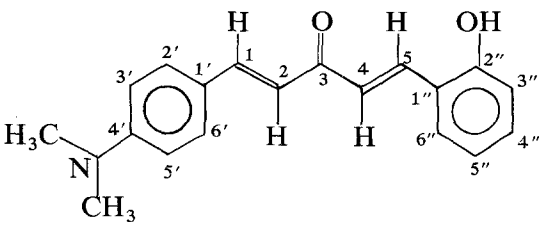

*s-cis, trans* **(II)**




*s-cis, cis* **(III)**

phenyl]-penta-1,4-dien-3-one is drawn in **(IV)** as the *s-trans, trans* conformer, showing the chemical numbering. Crystallographic numbering is shown in Figure 5.

DHDK · 0.4 $CHCl_3$ is thus a clathrate inclusion complex. It seems that low temperature measurements will be needed to properly define the situation of the $CHCl_3$ molecule in its cavity.




*s-trans, trans* **(IV)**

### 3.2. CRYSTAL STRUCTURE OF DHDK · *m*-DINITROBENZENE

A stereodiagram of the crystal structure is shown in Figure 2. We note first that the DHDK molecule has a different conformation from that found in the Group I complexes and in DHDK · PDMB (see Section 3.3) – the molecule here has an *s-cis, trans* conformation. The DHDK molecules are hydrogen-bonded through arbonyl – hydroxyl interactions, ($d$(O...O) = 2.64(1) Å) in chains in the $y$ direction. Both components lie in the molecular sheet in (201). Such a sheet is shown in Figure 3, where two ribbons of like molecules extending along $y$ are shown (see the Appendix for a discussion of the symmetry of this figure).

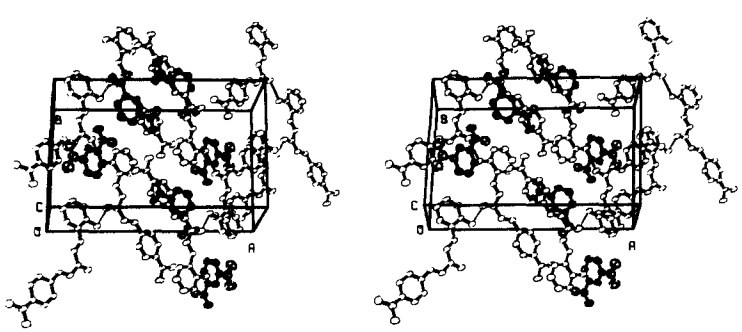


Fig. 2. DHDK · *m*-dinitrobenzene-stereodiagram of the crystal structure. For clarity, the two components have been represented differently.

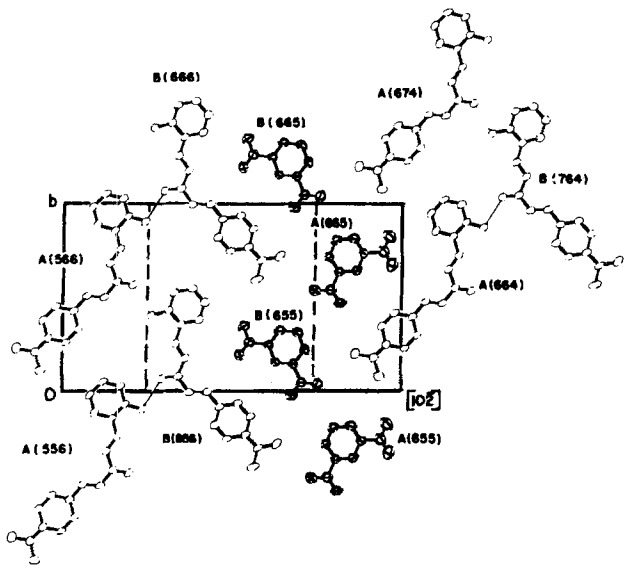



Fig. 3. DHDK · *m*-dinitrobenzene – the sheet of molecules lying in (201). The two independent molecules of each type in the asymmetric unit are designated A and B. The reference molecules (coordinates in Table IV) are denoted as 555, translations along the crystal axes being specified by adding or subtracting integers from the reference code. (Cf. ORTEP system.) The rectangle shows the unit cell of the *pg* plane group, with its glide lines (see Appendix).

The DHDK ribbon is actually two DHDK molecules in width (A and B, the two molecules of the asymmetric unit) and the hydrogen bonding is head to waist, the sequence being A to B, B to A... etc. The *p*-dimethylamino portions of the DHDK molecules project from the DHDK ribbon and define a sinuous channel in which the two crystallographically-independent *m*-dinitrobenzene molecules (A, B) are included. The *m*-dinitrobenzene molecules interact with adjacent molecules (both DHDK and *m*-dinitrobenzene) by dispersion forces only. Adjacent sheets are mutually shifted so that DHDK molecules of one sheet lie above *m*-dinitrobenzene molecules of the next sheet and so on; portions of two sheets related by the centre of symmetry at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ are shown in Figure 2. Thus, this structure has some features of channel inclusion complexes; however, in the usual type of channel inclusion complex, the channel axes are linear while here the sinuous axis of the channel appears to be a novel feature.

### 3.3. CRYSTAL STRUCTURE OF DHDK · PDMB

A stereodiagram of the crystal structure (Figure 4) shows that the DHDK molecules (in the *s-trans, trans* conformation) form the sides of a channel of approximately rectangular cross-section, with their long axes perpendicular to the channel axis. The channel axes lie along [001] and the DHDK planes are approximately parallel to (110) and ($1\bar{1}0$). The PDMB molecules are contained in the channels and have their mean planes approximately perpendicular to those of the DHDK molecules; there is a hydrogen bond between the carbonyl oxygen of PDMB and hydroxyl of DHDK ($d$(O...O) = 2.724(8) Å).

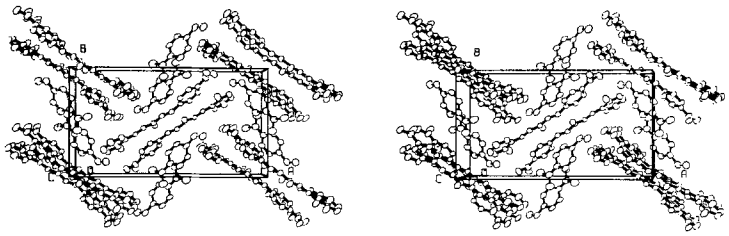


Fig. 4. DHDK · PDMB-stereodiagram of the crystal structure.

## 4. Geometrical Features of Host and Guest Molecules

### 4.1. GEOMETRY OF THE DHDK MOLECULE

Dimensions of the DHDK molecule in the extended *s-trans, trans* conformation as found in DHDK · PDMB are shown in Figure 5; similar but less accurate values obtained from the

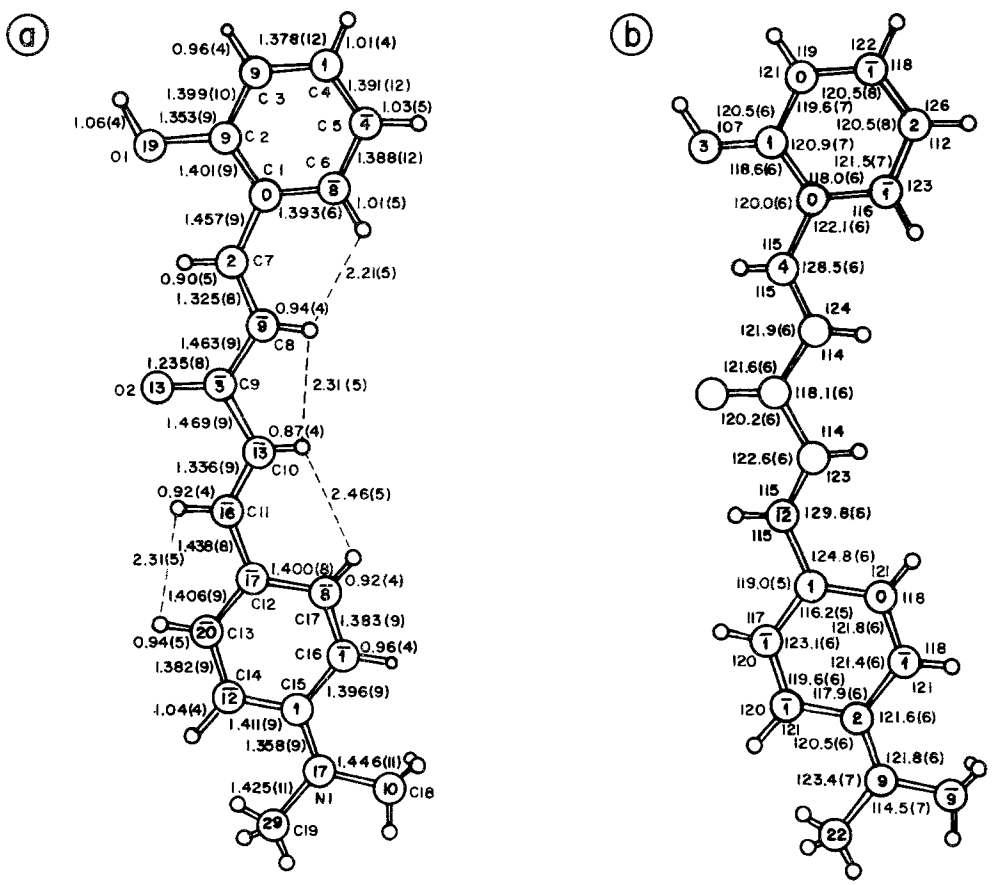



Fig. 5. DHDK · PDMB complex – dimensions of the DHDK molecule: (a) Bond lengths (Å) (not corrected for thermal vibrations), numbering of atoms and deviations (units of $10^{-2}$ Å) from the best plane of the molecule as a whole, (b) bond angles (deg) and deviations (units of $10^{-2}$ Å) from planes of the substituted phenyl groups (best planes are taken separately through the C atoms of the two benzene rings).

$CHCl_3$ complex are not reproduced. The lengths of the individual single and double bonds in the pentadienone chain conform to standard values, showing that there is little charge delocalization in this part of the molecule. The angles at C(7) and C(11) are appreciably greater than 120° and this probably results from the need to relieve strain caused by close approaches between hydrogen atoms. The DHDK molecule is both slightly bow-shaped and twisted with respect to its long axis.

Dimensions of the DHDK-A molecule in the *s-cis*, *trans* conformation as found in DHDK · *m*-dinitrobenzene are shown in Figure 6; the results for the B molecule are very similar and have been deposited. The bond lengths do not differ significantly from those found in DHDK · PDMB, despite the differences in conformation. The molecules A and B are both essentially planar (details of best planes through various groups of atoms have been deposited).

DHDK is a substituted dibenzylidene acetone (DBA), a well-known ligand in the formation of metal coordination complexes. Although the structure of DBA itself or derivatives has not

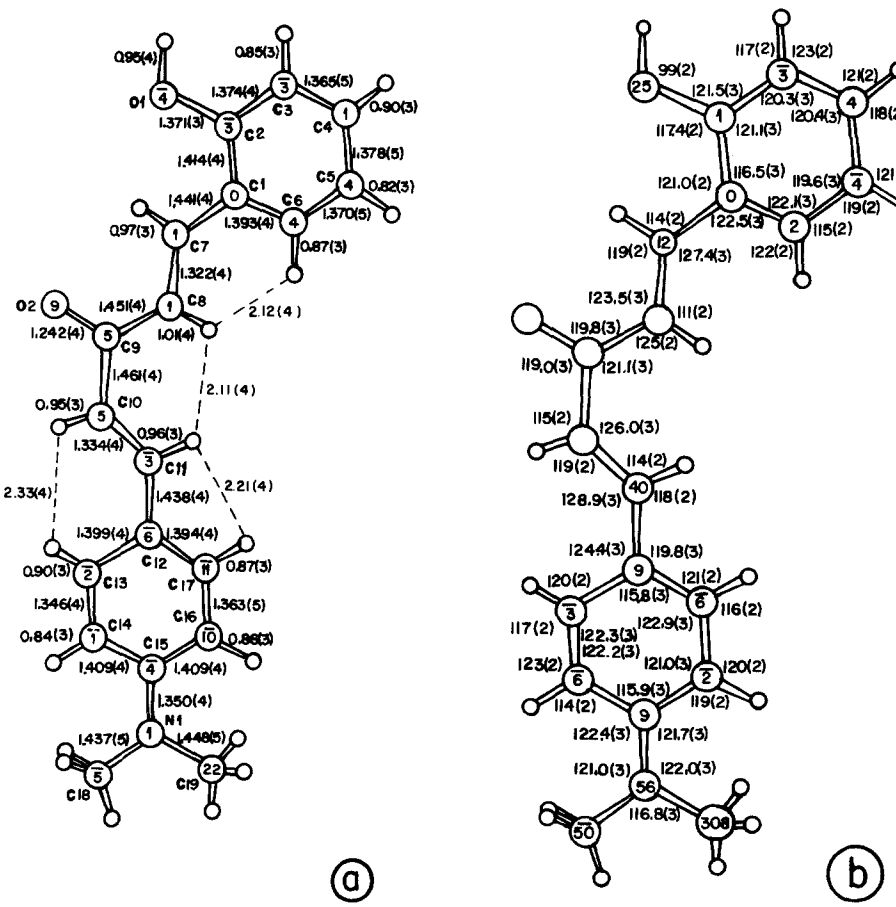



Fig. 6. DHDK · *m*-dinitrobenzene complex – dimensions of one (A) of the two crystallographically-independent DHDK molecules in the unit cell: (a) bond lengths (Å) (not corrected for thermal vibrations), and deviations (units of $10^{-2}$ Å) from the best plane of the molecule as a whole. (b) bond angles (deg) and deviations ($10^{-3}$ Å) from planes of the two substituted phenyl groups (best planes are taken separately through six C atoms of the two benzene rings). Analogous diagrams for molecule B have been deposited.

been reported, those of solvated complexes of $Pd_2(DBA)_3$ have been determined [9, 10]. Both *s-trans, trans(***I***)* and *s-cis, trans(***II***)*, see p. 243, conformers were found, linked to Pd via the C=C bonds. Conformational isomerism of DBA and analogues can also be compared with that of dithizone (1,5-diphenylthiocarbazone), where solid-state conformation analogues to **I** (e.g., in dithizone itself [11] and in dithizone · $I_2$ [12]), **II** (e.g., in *S*-methyldithizone [13] and **III** (e.g., 1,5-bis(2,6-dimethylphenyl)-3-nitroformazan [14]) have been found. Steric hindrance between HC(1) and HC(5) (chemical numbering) makes conformation **III** unlikely in DBA derivatives but one of these hydrogens is absent in the dithizone analogues.

Comparison can also be made with piperine [15, 16] and wisanine [17], which both contain penta-1,3-diene-5-one chains. Their covalent parameters resemble those of the *s-trans, trans* penta-1,4-diene-3-one chain in DHDK.

### 4.2. GEOMETRY OF THE *m*-DINITROBENZENE MOLECULE

The dimensions of the two independent *m*-dinitrobenzene molecules in the DHDK complex are very similar; the only significant differences are in the dispositions of the nitro groups with respect to the benzene rings and we ascribe these to packing effects. Our values for bond-lengths and angles are very close to the values obtained for *m*-dinitrobenzene itself [18] (details deposited; we compare values uncorrected for thermal motion, the thermal motion corrections being $\sim 0.01$ Å on bond lengths). The two electron-withdrawing nitro groups have little effect on the bond lengths in the benzene ring, but the *ipso* bond angle (at the carbons to which $NO_2$ is bonded) is increased to 122.2°. This value is very close to that found in *para*-substituted nitrobenzenes [19]; this is generally ascribed to changes in the hybridization of the *ipso* carbon atom. The value of 124° found for $\measuredangle$ ONO is usual for $d(C-N) = 1.48$ Å. There appears to be little $\pi$-conjugation between the nitro groups and the benzene ring.

### 4.3. STRUCTURE OF THE PDMB MOLECULE

Dimensions are given in Figure 7. To our knowledge, the structure of PDMB has not been determined, although crystal cell dimensions have been reported [20]. The dimensions of the aldehyde portion of *p*-hydroxybenzaldehyde [21] agree well with our values for that region of PDMB.

The dimensions of the dimethylamino substituted benzene ring can be discussed for the DHDK and PDMB molecules together, as there is an appreciable resemblance (details deposited). This benzene ring has an appreciable amount of *p*-quinoidal character, with the *quasi* single and double bonds having lengths of $\sim 1.40$ and 1.36 Å, respectively, and bond angles of $\sim 117$ and $\sim 116°$ at the substituted carbon atoms (the former for the $N(CH_3)_2$ substituted carbon). The comparable values in *p*-benzoquinone (at $-160\,°C$) are 1.477(3), 1.334(3) Å and 118.2(1)° [22] so there is clearly more $\pi$-electron delocalization in the DHDK and PDMB benzene rings than in *p*-benzoquinone. The decrease in the interior angles at the substituted carbons is partly due to the quinoidal character of the ring and partly to the change in hybridization that results from the electron donor character of the $N(CH_3)_2$ substituent. The $N(CH_3)_2$ groups encountered in this study have trigonal planar hybridization but those in neutral *N,N,N′,N′*-tetramethylphenylenediamine [23, 24] have a degree of pyramidal bonding (sum of nitrogen bond angles is 352(1)°); the carbon ring is benzenoid rather than quinonoid.

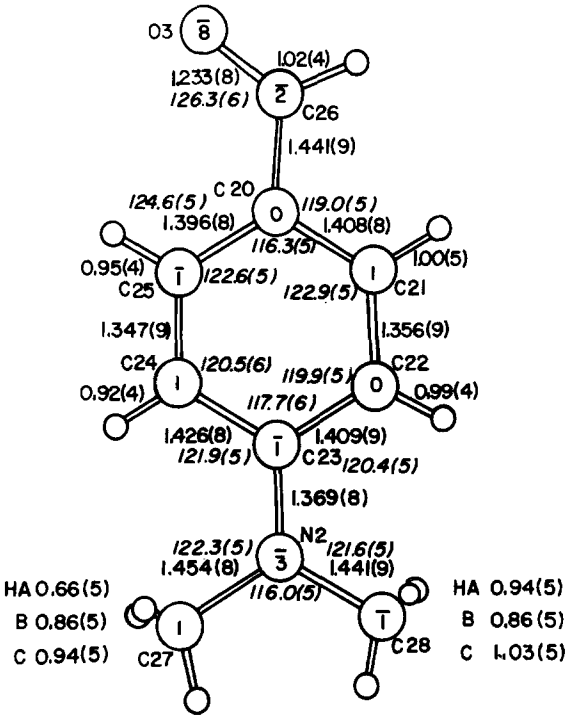



Fig. 7. DHDK · PDMB complex – dimensions of the PDMB molecule – bond lengths (Å) (not corrected for thermal vibrations), bond angles (deg) and deviations (units of $10^{-2}$ Å) from the best plane through C atoms of the benzene ring.

## 5. Comparison of Host-Guest Arrangements in the Three Types of Complex

In the present study we have found three different structural types of DHDK complexes. The DHDK · 0.4 $CHCl_3$ complex belongs to the clathrate group with the guest molecules completely enclosed by the surrounding host framework, the $CHCl_3$ molecules being disordered in their cavities. The DHDK · 0.5 $C_2H_5OH$ complex is isomorphous and DHDK · $CH_3COOH$ also belongs to this general group of structures. On the other hand, DHDK · PDMB has a channel-type structure, stabilized by host-guest hydrogen bonding. Finally DHDK · *m*-dinitrobenzene can be classified as a channel inclusion complex of novel type, with host and guest molecules arranged together in a planar sheet, the guests being accommodated in curvilinear channels between the hydrogen-bonded host molecules. From the powder photographs we infer that DHDK · anisaldehyde has a similar structure.

The variety of structural types found among the DHDK molecular complexes stems from the ability of the host molecule to activate different types of functionalities in its encounters with different kinds of guests. The DHDK molecule has the following features important in the formation of complexes:

(i) An ability to adjust its conformation to suit the shape of guests. This is a necessary but not sufficient condition because the methoxy analogue of DHDK (with similar conformational possibilities) does not form inclusion complexes.

(ii) A complicated shape which makes close packing of the molecules difficult; the voids that appear can then be occupied by guest molecules.

(iii) DHDK contains a hydrogen-bond donor in its hydroxyl group and a hydrogen-bond acceptor in its carbonyl group. Thus DHDK can be expected to form hydrogen bonds both with other DHDK molecules and also to act as acceptor or donor in hydrogen bonding with guest molecules.

(iv) DHDK contains both electron donor (*p*-dimethylaminophenyl) and acceptor (*o*-hydroxyphenyl) portions and these can form $\pi - \pi^*$ charge-transfer compounds with electron acceptors or donors, respectively. The TNB and TNT molecular compounds of DHDK are presumably examples in which it behaves as an electron donor.

Points (i)–(iii) are nicely reflected in the three structures reported here. Two modes of host–host hydrogen bonding have been found. Centrosymmetric pairs of DHDK molecules are formed in the DHDK · 0.4 $CHCl_3$ clathrate; these molecule-pairs interact *via* van der Waals forces, among which we include local dipole–dipole interactions. The hydrogen bonding in DHDK · *m*-dinitrobenzene leads to long chains of DHDK molecules; here continuous channels rather than separated cavities occur which are filled by the guest molecules, giving planar binary sheets. Finally, host-guest hydrogen bonding occurs in DHDK · PDMB, where the major host-host interaction appears to be from dipole–dipole interactions between DHDK molecules aligned in the walls of the channels.

Such versatility in the formation of molecular complexes through the expression of various functionalities in the complex-forming molecule is a well-known feature. For example, thiourea forms channel inclusion complexes based on S···H–N hydrogen bonding, and metal coordination complexes of various types depending on the nature of the metal. On the other hand, such versatility should be contrasted with the tendency of some complex-forming molecules to form structures of a uniform type with chemical selectivity towards the guest molecules. An example of this type is provided by *N*-(*p*-tolyl)-tetrachlorophthalimide, where the complexes are (almost) all isomorphous channel inclusion complexes and the guests all have aromatic character [25]. However, even here there is a limit to the restrictiveness because it seems that $\pi$–$\pi^*$ charge transfer complexes can be formed when the aromatic guest molecule is too large to enter the channels of the inclusion-type structure.

Heilbron and Buck [1] reported a variety of different colours for the complexes that they prepared. We have not been able to reproduce these, all our complexes are deeply coloured, and appear red when viewed in thin section by transmission. The intense colour seems likely to be an intrinsic property of the DHDK molecule, the light absorption resulting from charge transfer interactions between donor and acceptor portions; these intramolecular transitions appear to be only slightly influenced by the second component of the molecular complex.

## Appendix: Additional symmetry in (201) molecular sheets of DHDK · *m*-dinitrobenzene

Inspection of Figure 3 shows that the crystallographically-independent A and B molecules are related by *b* glide planes. A non-reduced unit cell (with the same volume as the reduced cell of Table I) can be defined by the vectors **a**-2**c**, **b**, **c** of the reduced cell. This cell has $a' = 25.55$, $b' = 13.85$, $c' = 7.76$ Å, $\alpha' = 82.28$, $\beta' = 121.90$, $\gamma' = 90.07°$. The rectangle outlined in Figure 3 has sides parallel to $a'$, $b'$ but its origin has been shifted from the centre of symmetry to the molecular layer. Because of the mutual shift of adjacent layers the glide is not a symmetry element of the lattice. The molecular layers have two-dimensional space group symmetry *pg* (Vol. IV of *International Tables for X-ray Crystallography* (1965)).

Additional symmetry in two-dimensional layers (but which does not extend to the three-dimensional lattice) has been noted in 5-fluorouracil [27] and 9-ethylguanine HCl [28] and in a slightly different sense, also in (theobromine)$_2 \cdot H_2I_8$ [29].

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