Table 2. *Selected geometric parameters (Å, °)*

C2—C3	1.435 (4)	C5—O3	1.363 (3)
C4—C10	1.437 (3)	C7—O4	1.360 (3)
C5—C6	1.369 (3)	O3—C11	1.427 (4)
C5—C10	1.406 (3)	O4—C12	1.418 (4)
O1—C2—C3	116.7 (2)	O1—C9—C8	115.9 (2)
O1—C2—O2	116.2 (2)	C8—C9—C10	124.1 (2)
O2—C2—C3	127.0 (2)	C5—C10—C9	117.2 (2)
C7—C8—C9	115.9 (2)	C4—C10—C5	124.5 (2)

Data were corrected for Lorentz and polarization effects. The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1985). Isotropic refinement of the structure by least-squares methods using *SHELXL*93 (Sheldrick, 1993) was followed by anisotropic refinement of all the non-H atoms. All H atoms were located from a difference Fourier map and their positions and isotropic displacement parameters were refined (except U_{iso} of the two methyl groups of the side chain located at C8). All calculations were performed on a PC/AT-386 computer.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: locally written program. Program(s) used to solve structure: *SHELXS*86 (Sheldrick 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: VJ1039). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The Charge-Transfer Complex 4-(2-Hydroxyethyl)carbazole–2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (1/1) (HEK–DDQ)

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Abstract

The planar donor HEK and the nearly planar acceptor DDQ dimerize to form a face-to-face alternately arranged π–π charge-transfer complex, $C_{14}H_{13}NO.C_8Cl_2N_2O_2$.

Comment

The electron acceptor, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), possesses a uniquely high electron affinity of 3.13 eV (Chen & Wentworth, 1975) and can react with various electron donors to form charge-transfer complexes with different structural types. BPH–DDQ (BPH = benzo[*c*]phenanthrene) adopts a mixed-stack packing motif, with many short intermolecular distances between the parallel molecular planes of two adjacent BPH and DDQ molecules typical of π–π intermolecular interactions (Bernstein, Regev & Herbstein, 1977). PH (PH = phenanthrene) and DDQ in PH–DDQ are arranged in a similar way but with no short intermolecular contacts (Herbstein, Kapon, Rzonzew & Rabinovich, 1978). DAPH (DAPH = diazaphenanthrene) and DDQ in $(DAPH)_2$–DDQ are arranged in segregated sheets with the DAPH and DDQ planes perpendicular to each other, corresponding to an n–π electronic interaction mode, that is coordinating the DAPH lone pair of electrons with the π orbital of DDQ (Shaanan, Shmueli & Colapietro, 1982). Recently, it was reported that 4-(2-

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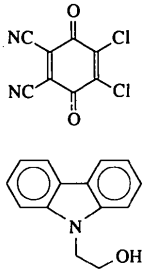
hydroxyethyl)carbazole (HEK) exhibits interesting photoconductive and non-linear optical properties (Wada, Zhang, Choi & Sasabe, 1993), this paper also describes the crystal structure but gives no detail of the molecular geometry. In view of the possibility that HEK and DDQ may form photoconductive charge-transfer complexes, we synthesized the title complex, (I), and its structural features are described here.



(I)

Two benzene rings of HEK are slightly bent away from the central five-membered planar ring in the same direction, forming dihedral angles of 2.9 (1) and 1.4 (1)°, respectively. Although C13 has a deviation of 0.190 Å from the least-squares plane of the carbazole moiety (C1,C2,...,C12,N1), the sum of angles around N1 is 357.8 (3)° indicating that the N1 atom is not far from being sp^2 hybridized. The C13—N1 bond is slightly shortened from a single bond while C6—N1 and C8—N1 have more double-bond character. These bond lengths and angles, combined with the demand of the aromatic $4n+2$ rule, indicate that N1 contributes two electrons to the HEK π-delocalized molecular orbital, rendering n–π intermolecular interactions impossible.

As in all reported donor–DDQ complexes, the deviation from planarity of DDQ in HEK–DDQ is significant but smaller than that of neutral DDQ (Zanotti, Bardi & Del Pra, 1980) or monoanionic DDQ^- in $TPA^+.DDQ^-$ (Marzotto, Clemente & Pasimeni, 1988). The average values of the two C=O bond lengths in DDQ, HEK–DDQ, and $TPA^+.DDQ^-$ are 1.203 (3), 1.213 (5) and 1.258 (4) Å, respectively, and the means of the corresponding C—C(O) bonds are 1.497 (4), 1.484 (6) and 1.438 (4) Å, respectively. Thus, on reducing $DDQ^{\delta-}$ from $\delta = 0$ to $\delta = 1$, the C=O bond appears to lengthen and the neighbouring C—C bond to shorten. This variation is in accord with the results of Miller & Dixon (1987) for another series of $(DDQ)^{n-}$ complexes.

HEK and DDQ form a face-to-face dimer characterized by many short C···C and C···N intermolecular atomic contacts as shown in Table 3. The least-squares planes through C1,C2,...,C12,N1 of HEK and DDQ are almost parallel, the dihedral angle being 6.4°. Thus, the preferred mode of interaction between HEK and DDQ is π–π. The intermolecular interactions between dimers are comparatively weak with only one short C21···C11($1-x$, $1-y$, $-z$) distance of 3.36 (1) Å.

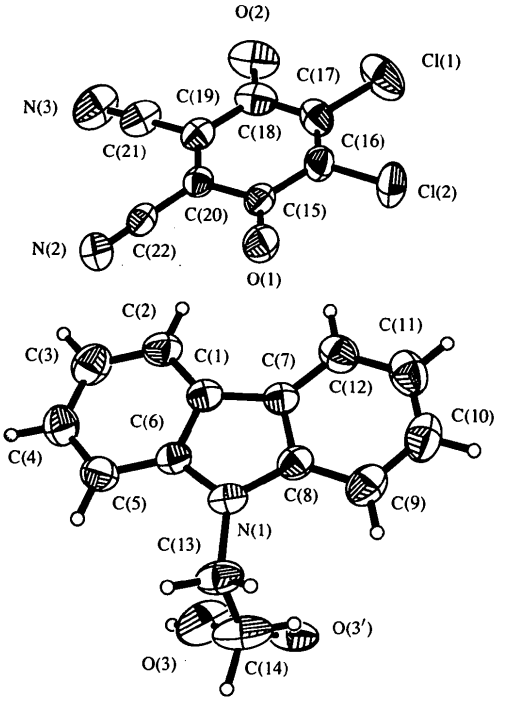


Fig. 1. Molecular structure showing 50% probability displacement ellipsoids. O3 and O3′ represent the two components of disorder.

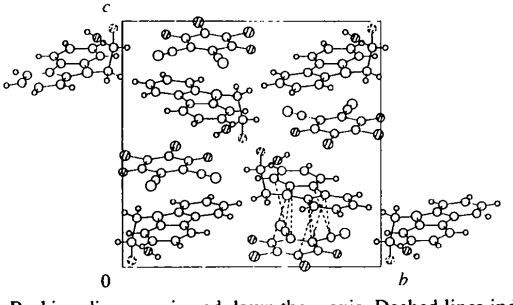


Fig. 2. Packing diagram viewed down the *a* axis. Dashed lines indicate short intermolecular distances in one asymmetric unit.

Experimental

Under an Ar atmosphere, 0.5 mmol colourless HEK was added to a 10 ml DDQ/CH_3CN solution of 0.5 mmol DDQ with stirring. The orange solution immediately turned blue. After the solution was condensed in a vacuum dryer overnight, blue–green parallelepipeds of HEK–DDQ crystallized out. Yield: 69%, m.p. 407–409 K.

Crystal data

$C_{14}H_{13}NO.C_8Cl_2N_2O_2$
M_r = 438.27
Monoclinic
$P2_1/c$
a = 8.785 (4) Å
b = 15.306 (7) Å
c = 14.573 (3) Å
β = 97.00 (3)°

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 3–12°
μ = 0.37 mm^{-1}
T = 293 K
Parallelepiped

V = 1945 (1) Å^3
Z = 4
D_x = 1.50 Mg m^{-3}
D_m not measured

0.3 × 0.2 × 0.2 mm
Blue–green

Data collection

Nicolet *R3m/E* diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3931 measured reflections
3847 independent reflections
2237 observed reflections [$F > 4\sigma(F)$]

R_{int} = 0.015
θ_{max} = 25°
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 19$
$l = -18 \rightarrow 18$
2 standard reflections monitored every 100 reflections
intensity decay: <5%

Refinement

Refinement on F
R = 0.0614
wR = 0.0640
S = 1.588
2237 reflections
285 parameters
H atoms: see text
$w = 1/[\sigma^2(F) + 0.0009F^2]$
$(\Delta/\sigma)_{max}$ = 0.35
$\Delta\rho_{max}$ = 0.39 e Å^{-3}
$\Delta\rho_{min}$ = −0.62 e Å^{-3}

Extinction correction: *SHELXTL* (Sheldrick, 1985)
Extinction coefficient: χ = 0.0007
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cl1	0.9269 (1)	0.7049 (1)	0.0041 (1)	0.089 (1)
Cl2	0.8312 (1)	0.5100 (1)	0.0435 (1)	0.080 (1)
O1	0.5358 (3)	0.5021 (2)	0.1121 (2)	0.058 (1)
O2	0.6970 (4)	0.8310 (2)	0.0528 (2)	0.075 (1)
O3	0.0233 (5)	0.0989 (3)	0.0654 (3)	0.088 (2)
O3′	0.1701 (13)	0.0350 (7)	0.0286 (6)	0.062 (5)
N1	0.2790 (3)	0.1361 (2)	0.2055 (2)	0.041 (1)
N2	0.2117 (4)	0.6108 (2)	0.1675 (2)	0.062 (1)
N3	0.3373 (5)	0.8607 (2)	0.1369 (3)	0.082 (2)
C1	0.3265 (4)	0.2826 (2)	0.2046 (2)	0.040 (1)
C2	0.2917 (5)	0.3706 (3)	0.2169 (3)	0.051 (1)
C3	0.1535 (5)	0.3912 (3)	0.2477 (3)	0.062 (2)
C4	0.0488 (5)	0.3262 (3)	0.2647 (3)	0.058 (2)
C5	0.0796 (4)	0.2398 (3)	0.2529 (3)	0.050 (1)
C6	0.2200 (4)	0.2176 (2)	0.2228 (2)	0.038 (1)
C7	0.4524 (4)	0.2381 (2)	0.1694 (2)	0.038 (1)
C8	0.4185 (4)	0.1482 (2)	0.1696 (2)	0.040 (1)
C9	0.5142 (5)	0.0853 (3)	0.1387 (3)	0.054 (1)
C10	0.6485 (5)	0.1157 (3)	0.1078 (3)	0.065 (2)
C11	0.6861 (5)	0.2037 (3)	0.1085 (3)	0.061 (2)
C12	0.5905 (4)	0.2655 (3)	0.1393 (3)	0.052 (1)
C13	0.1921 (5)	0.0546 (2)	0.1997 (3)	0.050 (1)
C14	0.1218 (6)	0.0340 (3)	0.1038 (3)	0.073 (2)
C15	0.5737 (4)	0.5766 (2)	0.0983 (2)	0.043 (1)
C16	0.7198 (4)	0.5977 (3)	0.0627 (3)	0.051 (1)
C17	0.7602 (4)	0.6798 (3)	0.0477 (3)	0.053 (1)
C18	0.6626 (5)	0.7557 (3)	0.0667 (2)	0.054 (1)
C19	0.5160 (4)	0.7346 (2)	0.1027 (2)	0.045 (1)
C20	0.4726 (4)	0.6508 (2)	0.1161 (2)	0.040 (1)
C21	0.4179 (5)	0.8063 (2)	0.1208 (3)	0.056 (1)
C22	0.3290 (4)	0.6292 (2)	0.1452 (2)	0.044 (1)

Table 2. *Selected geometric parameters (Å, °)*

O3—C14	1.390 (6)	N3—C21	1.136 (6)
N1—C8	1.402 (5)	C15—C20	1.483 (5)
C1—C7	1.445 (5)	C18—C19	1.484 (6)
Cl1—C17	1.709 (4)	C20—C22	1.418 (5)
N2—C22	1.151 (5)	N1—C6	1.385 (5)
C15—C16	1.478 (5)	C1—C6	1.413 (5)
C17—C18	1.489 (6)	C13—C14	1.492 (6)
C19—C21	1.440 (5)	O1—C15	1.211 (4)
O3′—C14	1.222 (11)	O2—C18	1.215 (5)
N1—C13	1.459 (5)	C16—C17	1.331 (6)
C7—C8	1.409 (5)	C19—C20	1.359 (5)
Cl2—C16	1.704 (4)		
C6—N1—C8	108.2 (3)	C6—N1—C13	125.1 (3)
C8—N1—C13	124.5 (3)	C2—C1—C6	119.6 (3)
C2—C1—C7	133.5 (3)	C6—C1—C7	106.7 (3)
N1—C6—C1	109.2 (3)	N1—C6—C5	129.7 (3)
C1—C6—C5	121.1 (3)	C1—C7—C8	106.8 (3)
C1—C7—C12	134.3 (3)	C8—C7—C12	118.9 (3)
N1—C8—C7	108.9 (3)	N1—C8—C9	128.3 (3)
C7—C8—C9	122.7 (3)	O1—C15—C16	122.1 (3)
O1—C15—C20	120.6 (3)	Cl2—C16—C15	115.2 (3)
Cl2—C16—C17	123.2 (3)	Cl1—C17—C16	122.0 (3)
Cl1—C17—C18	115.7 (3)	O2—C18—C17	123.2 (4)
O2—C18—C19	120.7 (4)	C18—C19—C21	117.6 (3)
C20—C19—C21	120.6 (4)	C15—C20—C19	120.8 (3)
C15—C20—C22	116.5 (3)	C19—C20—C22	122.6 (3)
N3—C21—C19	177.3 (5)	N2—C22—C20	178.8 (4)

Table 3. *Contact distances (Å)*

C19···C1^{i}	3.07 (1)	C18···C1^{i}	3.35 (1)
C21···C1^{i}	3.20 (1)	C20···C7^{i}	3.39 (1)
C18···C5^{i}	3.26 (1)	C21···C11^{ii}	3.36 (1)
C19···C7^{i}	3.30 (1)	C18···C6^{i}	3.17 (1)
C17···C6^{i}	3.38 (1)	C19···C6^{i}	3.24 (1)
C20···N1^{i}	3.19 (1)	C21···C7^{i}	3.30 (1)
C20···C8^{i}	3.15 (1)	C22···C9^{i}	3.35 (1)
C17···C5^{i}	3.20 (1)	C15···N1^{i}	3.13 (1)
C22···C8^{i}	3.29 (1)		

Symmetry codes: (i) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $1 - x, 1 - y, -z$.

A difference Fourier synthesis showed an additional peak of 1.5 e Å^{-3} near C14 and O3; the latter atom also exhibited large anisotropic displacement parameters. These factors indicated O3 to be disordered. The second component is denoted as O3′ and interpreted as the O atom of the aldehyde group which originated from the dehydrogenation of the hydroxy group under the combined influence of DDQ and the *in situ* Mo $K\alpha$ X-ray radiation. DDQ is a well known dehydrogenating agent, but the dehydrogenation of HEK would not be expected to take place without irradiation. The ^{1}H NMR signals of the hydroxyethyl of HEK are the same as those of HEK–DDQ and the mass spectroscopy of HEK–DDQ has an *m/z* peak corresponding to HEK. However, the IR ν(OH) band of HEK–DDQ/KBr which had undergone 24 h of irradiation was considerably weaker than that of the same sample without irradiation. The unrestrained bond lengths (C14—O3 1.30, C14—O3′ 1.09 Å) are not equivalent suggesting that the disorder of O3 is more likely to result from the scrambling of C=O and C—OH groups than from any kind of dynamic disorder in the 'tail' of the hydroxyl groups. By restraining the C14—O3 distance to 1.43 (3) Å and C14—O3′ to 1.22 (3) Å and by initializing the site-occupation factors to 0.5 for both O3 and O3′, the C14—O3 and C14—O3′ bonds were refined to 1.390 (6) Å and 1.222 (11) Å, respectively, with final occupation factors of 0.76 (O3) and 0.24 (O3′). One H atom (H14A) attached to C14 was located from a difference Fourier map and its positional parameters were refined, but

the other H atom could not be located because of the disorder. All other H atoms were fixed at ideal positions.

Data collection: Nicolet *P*3 software (Nicolet XRD Corporation, 1985). Cell refinement: Nicolet *P*3 software. Data reduction: *SHELXTL* (Sheldrick, 1985). Program(s) used to solve structure: *SHELXTL*. Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1017). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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β-Cyclodextrin Nonanoic Acid 1:1 Complex

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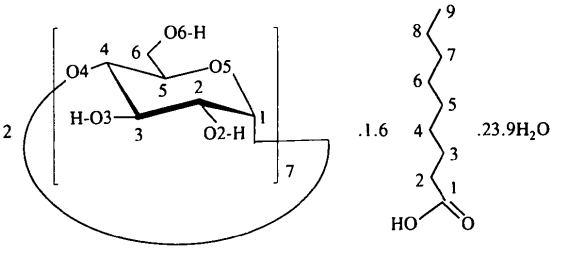
(Received 20 October 1995; accepted 12 February 1996)

Abstract

The structure of the complex of cyclomaltoheptaose (β-CD) with nonanoic acid, β-cyclodextrin–nonanoic acid (1/1) water solvate, $2C_{42}H_{70}O_{35}.1.6C_9H_{18}O_2.23.9H_2O$, has been determined at room temperature. Two independent molecules of β-CD form a dimer which encloses two molecules of nonanoic acid. The guest molecules penetrate the β-CD cavities to different depths. Their carboxylic groups point towards the primary hydroxyl region of β-CDs forming direct dimers through hydrogen bonds with the carboxylic groups of adjacent guests along the *a* axis and interact with water molecules and disordered primary hydroxyl O atoms.

Comment

The structure determination of the title compound, (I), is a part of a systematic investigation involving the inclusion of linear molecules by β-CD or its derivatives (Mentzafos, Mavridis & Schenk, 1994).



(I)

The numbering scheme for the host and guest molecules is given in Fig. 1; C(*A* or *B*)*mn* or O(*A* or *B*)*mn* denotes the *m*th atom within the *n*th glucosidic residue of the crystallographically independent β-CD molecules

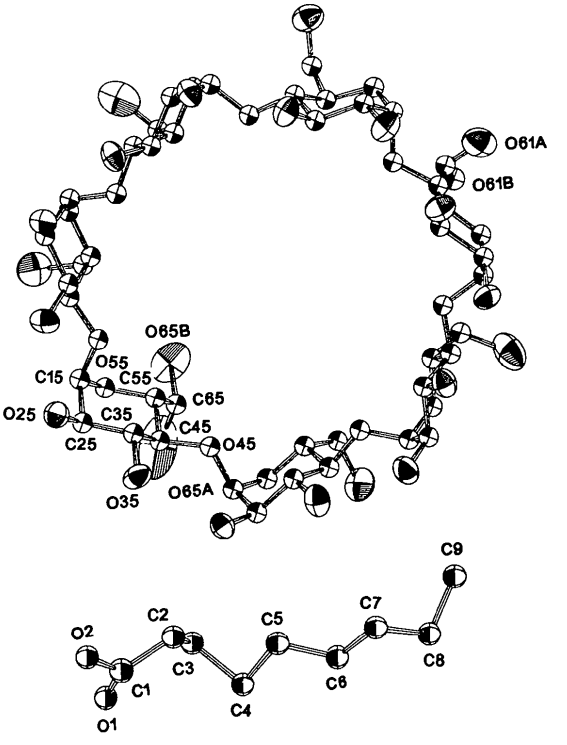


Fig. 1. The host and guest molecule *A* with the atomic numbering scheme. Displacement ellipsoids are plotted at the 50% level.

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