

Furan-Quinone Pigments. I. The Crystal and Molecular Structure of *N*-(2'-Pyridyl)-8,13-dioxodinaaphtho[2,1-*b*:2',3'-*d*]furan-6-carboxamide

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Crystals of *N*-(2'-pyridyl)-8,13-dioxodinaaphtho[2,1-*b*:2',3'-*d*]furan-6-carboxamide (DFC) are triclinic ($P\bar{1}$) and contain four molecules in a unit cell of dimensions $a = 7.429$ (2), $b = 19.868$ (6), $c = 13.108$ (4) Å, $\alpha = 88.89$ (2), $\beta = 97.21$ (3), $\gamma = 102.26$ (5)°. The three-dimensional data were recorded at $\lambda(\text{Cu}) = 1.5418$ Å by photometric and counter techniques. The structure was solved by Patterson methods and refined by full-matrix least-squares procedures to a conventional R of 0.079 for 5909 observed reflections. The two independent molecules, I and II, have the same bond distances and angles but somewhat different nearly planar configurations as a result of their dissimilar environments. Intramolecular hydrogen bonds (N-H...O in molecules I and II and C-H...O in molecule II) contribute to the stability of the observed molecular configurations. The molecules are joined laterally by a network of C-H...O interactions in which all but one carbonyl group participate to form puckered sheets extending along the [101] and [010] directions. Pairs of weak N-H...N intermolecular hydrogen bonds (3.25 Å) between amino and pyridyl nitrogen atoms on centrosymmetrically related molecules of type II join alternate sheets into double layers. The shortest interbond separation between neighboring double layers (3.26 Å) is generated by one of the quinone carbonyl groups of type II molecules across a center of symmetry. The other intersheet contacts occur between overlapping aromatic groups (pyridyl, naphthyl and naphthoquinone) separated by average perpendicular distances ranging from 3.33 to 3.46 Å and held together by strong π - π dispersion forces. The continuity in the stacking and the strength of the π - π overlap may account for the photoelectrophoretic sensitivity of the powdered material.

Introduction

N-(2'-Pyridyl)-8,13-dioxodinaaphtho[2,1-*b*:2',3'-*d*]furan-6-carboxamide (DFC), $\text{C}_{26}\text{H}_{14}\text{N}_2\text{O}_4$, is a yellow pigment which exhibits photoelectrophoretic (PEP) activity, *i.e.* crystalline particles of the pigment immersed in a dielectric medium will acquire a net negative surface charge and migrate toward the positively charged electrode upon irradiation by light of suitable wavelength in an applied electric field (Tulagin, 1969; Weinberger, 1969). The stable modification of its parent compound, α -[2,1]benzobrazanquinone or α -BBQ (Walker, Miller, Griffiths & Goldstein, 1972) is much less sensitive in the PEP mode than DFC (Tutihasi, 1972*a*). These differences in PEP behavior parallel the photoconductive properties of DFC and α -BBQ as evidenced in the charge transport measurements of Tutihasi (1972*a*, *b*) and the photoinjection studies of Pfister & Nielsen (1972). On the other hand, the electronic spectra of the two materials are very similar in the solid state (Walker, Kuder & Miller, 1970; Walker, Miller & Kuder, 1972; Pfister & Nielsen, 1972). A structural investigation of DFC and related pigments was therefore undertaken in order to determine how the photoconductivity of these materials and hence their PEP sensitivity depended on their crystal structures.

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Experimental section

A description of the synthesis of DFC and preliminary crystallographic data for the compound were reported earlier by Weinberger, Unger & Cherin (1969) (WUC). The crystals used in the present study were well-formed prisms which had hexagonal end faces, and were obtained by recrystallization from hot quinoline. Examination of Weissenberg and precession photographs revealed no systematic absences, thereby indicating that the space group was $P1$ or $P\bar{1}$, in agreement with the deductions of WUC. $P\bar{1}$ was shown to be the correct space group by the subsequent structure

Table 1. *Crystal data for DFC*

The primed values are those of Weinberger *et al.* (1969). Their indices (h', k', l') are related to the present ones by the expressions: $h' = k$, $k' = -h - l$, $l' = h$.

Formula: $\text{C}_{26}\text{H}_{14}\text{N}_2\text{O}_4$	F.W. 418.392
Triclinic: $P\bar{1}$, $Z = 4$,	$F(000) = 864$
$a = 7.429$ (2),	$b = 19.868$ (5),
$\alpha = 88.89$ (2),	$\beta = 97.21$ (3),
$V = 1976$ (1) Å ³ ,	$D_x = 1.481$ (1), $D_m = 1.484$ (5) g cm ⁻³ *
$a' = 19.95$ (1),	$b' = 14.28$ (2), $c' = 7.474$ (8) Å
$\alpha' = 113.80$ (5),	$\beta' = 102.66$ (5), $\gamma' = 85.28$ (5)°
$V' = 1901$ Å ³ ,	$D_x = 1.46$, $D_m = 1.46$ g cm ⁻³
Cu $K\alpha$: $\lambda = 1.5418$ Å, $\mu = 8.34$ cm ⁻¹	
Crystal No. 1: $0.30 \times 0.40 \times 0.34$ mm	
Crystal No. 2: $0.26 \times 0.35 \times 0.30$ mm	
Crystal No. 3: $0.32 \times 0.57 \times 0.40$ mm	

* Measured by flotation in a mixture of CH_2Cl_2 and CCl_4 .

determination. Accurate unit-cell parameters were obtained by least-squares refinement of settings measured at 19°C on a FACS-1 Picker autodiffractom-

eter with Cu $K\alpha$ radiation. These parameters are compared with those of WUC in Table 1, which summarizes the crystal data for DFC.

Table 2. *Final values of the fractional coordinates and thermal parameters for the non-hydrogen atoms in DFC*

The standard deviations are given in parentheses. All values have been multiplied by 10^4 . The temperature factor is of the form $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)]$.

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	-3663 (6)	4742 (3)	-1061 (3)	534 (25)	700 (29)	300 (18)	237 (21)	-74 (17)	-95 (18)
C(2)	-2806 (6)	5422 (2)	-908 (3)	648 (28)	592 (27)	272 (17)	284 (21)	-19 (17)	40 (17)
C(3)	-1779 (6)	5632 (2)	33 (3)	482 (22)	436 (21)	300 (17)	149 (16)	-2 (15)	31 (15)
C(4)	-1684 (5)	6136 (2)	778 (3)	320 (18)	411 (17)	262 (15)	108 (14)	-1 (13)	23 (14)
N(5)	-2487 (4)	4472 (2)	646 (2)	419 (18)	409 (15)	332 (15)	72 (13)	-51 (13)	18 (14)
C(6)	-3465 (6)	4291 (2)	-271 (3)	457 (23)	551 (25)	390 (20)	83 (18)	-80 (17)	-82 (18)
N(7)	-677 (4)	5272 (2)	1769 (2)	384 (17)	353 (15)	273 (14)	92 (13)	-67 (12)	74 (12)
C(8)	93 (5)	5890 (2)	2220 (3)	432 (21)	386 (17)	299 (16)	120 (16)	-49 (14)	38 (14)
C(9)	29 (5)	6442 (2)	1809 (2)	1143 (29)	374 (15)	396 (15)	150 (17)	-246 (17)	59 (12)
C(10)	990 (5)	5870 (2)	3310 (3)	336 (18)	357 (17)	282 (15)	54 (14)	6 (13)	38 (13)
C(11)	1259 (5)	6452 (2)	3906 (3)	353 (19)	392 (17)	369 (18)	80 (15)	0 (14)	55 (15)
C(12)	1986 (5)	6474 (2)	4966 (3)	281 (17)	388 (17)	346 (17)	11 (14)	34 (13)	-3 (14)
C(13)	2137 (6)	7083 (2)	5539 (3)	463 (22)	369 (21)	441 (21)	24 (16)	50 (17)	-32 (17)
C(14)	2761 (6)	7110 (2)	6572 (3)	524 (24)	491 (23)	399 (20)	-11 (18)	29 (18)	-152 (18)
C(15)	3255 (6)	6537 (2)	7060 (3)	549 (26)	591 (27)	303 (18)	13 (20)	-19 (17)	-66 (18)
C(16)	3145 (5)	5936 (2)	6526 (3)	383 (20)	465 (21)	292 (17)	19 (16)	-28 (14)	-23 (15)
C(17)	2503 (4)	5888 (2)	5457 (2)	252 (17)	389 (17)	270 (15)	-6 (13)	19 (12)	2 (14)
C(18)	2300 (4)	5289 (2)	4834 (2)	241 (17)	362 (17)	288 (15)	33 (13)	-14 (12)	45 (13)
C(19)	1573 (4)	5304 (2)	3807 (2)	264 (17)	358 (17)	279 (15)	43 (13)	-19 (12)	8 (13)
C(20)	1481 (3)	4692 (1)	3318 (2)	353 (13)	343 (11)	223 (10)	84 (10)	-70 (9)	2 (9)
C(21)	2127 (5)	4274 (2)	4044 (2)	296 (17)	365 (17)	262 (15)	57 (13)	-23 (12)	56 (13)
C(22)	2644 (4)	4599 (2)	4974 (2)	257 (17)	368 (17)	278 (15)	37 (13)	-10 (12)	12 (13)
C(23)	3384 (5)	4219 (2)	5848 (3)	288 (18)	480 (19)	286 (16)	95 (15)	-39 (13)	59 (15)
C(24)	3379 (5)	3477 (2)	5658 (3)	283 (18)	431 (19)	357 (17)	72 (14)	6 (13)	100 (15)
C(25)	3958 (6)	3084 (2)	6476 (3)	480 (24)	553 (25)	392 (20)	170 (19)	35 (17)	113 (18)
C(26)	3937 (7)	2394 (3)	6333 (4)	601 (28)	575 (27)	576 (26)	244 (21)	85 (21)	215 (22)
C(27)	3294 (7)	2086 (2)	5372 (4)	584 (28)	463 (25)	698 (30)	214 (21)	117 (23)	168 (22)
C(28)	2757 (6)	2473 (2)	4548 (3)	472 (23)	445 (23)	509 (22)	126 (18)	53 (18)	46 (18)
C(29)	2788 (5)	3167 (2)	4680 (3)	325 (19)	381 (17)	384 (18)	61 (15)	-12 (14)	49 (15)
C(30)	2207 (5)	3569 (2)	3778 (3)	342 (18)	371 (17)	316 (16)	43 (14)	-21 (13)	2 (13)
O(31)	3957 (5)	4482 (2)	6692 (2)	745 (22)	603 (17)	286 (14)	203 (16)	-192 (13)	-29 (12)
O(32)	1832 (4)	3351 (1)	2902 (2)	651 (19)	428 (15)	348 (14)	87 (13)	-84 (12)	-54 (10)
C(1')	-4771 (6)	154 (3)	-6876 (3)	552 (27)	740 (31)	287 (19)	21 (22)	-89 (18)	-52 (19)
C(2')	-4861 (7)	753 (3)	-6393 (3)	592 (29)	697 (31)	462 (24)	213 (23)	-206 (20)	38 (22)
C(3')	-3665 (6)	975 (2)	-5498 (3)	577 (26)	526 (25)	388 (21)	179 (20)	-130 (19)	3 (18)
C(4')	-2447 (5)	565 (2)	-5127 (3)	382 (20)	430 (19)	284 (16)	47 (16)	-22 (14)	16 (14)
N(5')	-2321 (5)	-13 (2)	-5586 (2)	421 (19)	540 (21)	356 (16)	100 (16)	-34 (14)	-69 (14)
C(6')	-3492 (6)	-207 (2)	-6446 (3)	487 (24)	663 (27)	302 (18)	51 (20)	-27 (17)	-122 (18)
N(7')	-1221 (4)	708 (2)	-4201 (2)	400 (17)	427 (15)	324 (15)	140 (13)	-83 (12)	-31 (12)
C(8')	-1150 (6)	1217 (2)	-3511 (3)	498 (22)	396 (21)	301 (16)	152 (16)	-62 (15)	-13 (15)
O(9')	-1995 (5)	1674 (2)	-3660 (2)	1046 (28)	626 (21)	487 (17)	523 (20)	-319 (18)	-194 (15)
C(10')	84 (5)	1205 (2)	-2506 (2)	352 (18)	393 (17)	251 (15)	95 (15)	8 (13)	6 (14)
C(11')	740 (5)	1813 (2)	-1978 (3)	386 (19)	361 (17)	348 (17)	113 (15)	30 (14)	14 (14)
C(12')	1807 (5)	1858 (2)	-990 (3)	295 (17)	385 (17)	321 (16)	61 (14)	42 (13)	-44 (14)
C(13')	2400 (5)	2506 (2)	-477 (3)	424 (21)	393 (21)	449 (21)	102 (16)	-14 (17)	-74 (17)
C(14')	3300 (6)	2549 (2)	504 (3)	446 (22)	427 (23)	481 (22)	43 (17)	-32 (18)	-130 (18)
C(15')	3672 (5)	1959 (2)	999 (3)	408 (21)	527 (23)	352 (18)	44 (17)	-55 (16)	-112 (17)
C(16')	3176 (5)	1327 (2)	525 (3)	351 (19)	421 (21)	324 (17)	46 (15)	-5 (14)	-31 (15)
C(17')	2209 (4)	1255 (2)	-485 (3)	266 (16)	342 (15)	298 (15)	51 (13)	30 (12)	-19 (14)
C(18')	1565 (4)	620 (2)	-1043 (2)	253 (16)	403 (17)	274 (15)	71 (13)	29 (12)	28 (14)
C(19')	547 (5)	618 (2)	-2005 (2)	316 (17)	331 (15)	261 (15)	50 (13)	10 (12)	-25 (12)
O(20')	-7 (3)	-34 (1)	-2414 (2)	411 (14)	345 (11)	230 (11)	52 (11)	-19 (9)	-6 (9)
C(21')	708 (5)	-449 (2)	-1709 (3)	367 (19)	366 (17)	259 (15)	71 (14)	8 (13)	31 (13)
C(22')	1650 (4)	-98 (2)	-866 (2)	299 (17)	331 (15)	277 (15)	40 (13)	24 (13)	-5 (13)
C(23')	2502 (5)	-473 (2)	-24 (3)	347 (18)	405 (17)	278 (16)	68 (15)	-1 (13)	-1 (13)
C(24')	2237 (5)	-1236 (2)	-175 (3)	293 (18)	417 (19)	384 (18)	95 (14)	94 (14)	87 (15)
C(25')	2915 (5)	-1626 (2)	628 (3)	394 (21)	524 (23)	430 (21)	122 (17)	78 (17)	107 (18)
C(26')	2688 (6)	-2327 (2)	519 (4)	440 (23)	494 (25)	642 (27)	170 (18)	110 (19)	203 (20)
C(27')	1789 (6)	-2655 (2)	-384 (3)	485 (24)	385 (23)	741 (31)	129 (18)	109 (21)	97 (20)
C(28')	1087 (5)	-2280 (2)	-1181 (3)	400 (22)	444 (23)	557 (24)	68 (17)	75 (18)	-7 (19)
C(29')	1300 (5)	-1571 (2)	-1081 (3)	377 (20)	362 (17)	422 (20)	57 (15)	83 (16)	40 (15)
C(30')	477 (6)	-1184 (2)	-1934 (3)	478 (22)	381 (19)	345 (18)	13 (16)	43 (16)	-2 (15)
O(31')	3367 (5)	-198 (2)	767 (2)	861 (24)	517 (17)	373 (15)	187 (16)	-210 (15)	-31 (13)
O(32')	-316 (5)	-1436 (2)	-2743 (2)	1051 (28)	396 (15)	422 (16)	67 (16)	-194 (17)	-110 (13)

Data collection

Two different crystals were used to record integrated film data on multiple films with a Nonius integrating Weissenberg camera operated in equi-inclination geometry. The first crystal provided all hkl levels ($n=0-6$) accessible to Ni-filtered Cu $K\alpha$ radiation and the second, four hkn levels ($n=0-3$) with which to scale the first set. The data were measured with the aid of a Nonius microdensitometer (model II) and converted to net intensities I by the expression $I = \frac{1}{2} \log(B_1 B_2) - \log P$, where P is the minimum transmittance through the central plateau region of an integrated reflection and B_1, B_2 are the transmittance maxima recorded on either side of each reflection. The experimental error in the net intensity was taken as

$$\sigma_I = (\sigma_B/B)^2 + (\sigma_P/P)^2 + (\sigma_z/B)^2 [1 + (B/P)^2]$$

where σ_B and σ_P are the experimental errors in $B = \sqrt{B_1 B_2}$ and P , respectively, and σ_z is the error in the zero transmittance setting. Values of 0.05 were assigned to σ_B/B and 0.5 to σ_z . The multiple-film data for each level were placed on a common scale and averaged with the aid of these values of σ_I . Reflections for which I exceeded $2\sigma_I$ were classified as unobserved.

Following the application of the appropriate Lorentz-polarization factor (Buerger, 1960) and correction for absorption based on a multifaceted solid (Ahmed & Singh, 1967), the intensity measurements on different levels were correlated by the method of Hamilton, Rollett & Sparks (1965) to yield 5657 unique non-zero reflections. The structure was solved and partially refined on the basis of this data. Additional data covering the range in $(\sin \theta)/\lambda$ from 0.50 to 0.58 \AA^{-1} were subsequently measured on a Picker FACS-1 autodiffractometer from a third crystal of DFC with graphite-monochromatized Cu $K\alpha$ radiation. This set of data was corrected for Lorentz and polarization factors and for absorption as described in an earlier paper (Goldstein & Paton, 1973) and was averaged with the film data at the end of the isotropic least-squares refinement.

Structure determination and refinement

An attempt to deduce the structure of DFC with the aid of Long's (1965) sign determination program was unsuccessful. The structure was solved instead by a combination of three-dimensional Patterson and Fourier techniques. Least-squares refinement was carried out by full-matrix techniques with *Group 1*, the BNL version of *ORFLS* (Busing, Martin & Levy, 1962), which contains Doedens's (1970) modifications for rigid-group refinement. Initial values of the scale and overall temperature factors were deduced from the application of Wilson statistics to the E values (Karle & Karle, 1965). The atomic scattering factors were those from *International Tables for X-ray Crystallography* (1962) for neutral O, N and valence C atoms and

from Stewart, Davidson & Simpson (1965) for spherical H atoms.

The function minimized was $\sum w_i (|F_o| - K|F_c|)^2$, where K is a scale factor and w_i , the weight associated with the i th observational equation, had the functional form $w_i = 1$ for $|F_o| \leq 9$ and $w_i = (A + B|F_o| - C|F_o|^2)^{-1}$ for $|F_o| \geq 9$ with $A = 0.318$, $B = 0.0707$ and $C = 5.6 \times 10^{-4}$ (Cruickshank, 1970). The pyridyl rings and the two six-membered rings at the extremities of the benzobranquinone portions of each molecule were refined as rigid groups to facilitate the isotropic refinement. The hydrogen atoms were included in the structure factor calculations, first, in their calculated positions and later, in positions deduced from a difference Fourier map. During the course of the anisotropic refinement, fixed-atom contributions from the hydrogen atoms and one of the pyridyl groups had to be used in order to accommodate all the input parameters. Refinement was terminated when all calculated shifts were smaller than σ . The final values of the conventional agreement index $R = \sum |A| / \sum |F_o|$ and the weighted agreement index $R_w = (\sum w_i \Delta^2 / \sum w_i F_o^2)^{1/2}$ are 0.079 and 0.097, respectively, for 5909 unique non-zero reflections comprising both film and diffractometer data. The final value of $[\sum w_i \Delta^2 / (m - n)]^{1/2}$ is 0.851 for $m = 5909$ and $n = 577$.

The refined atomic parameters for the non-hydrogen atoms are given in Table 2. The positional and thermal parameters of the hydrogen atoms presented in Table 3 were obtained from a difference Fourier map calculated at the end of the least-squares refinement with all data having $(\sin \theta)/\lambda < 0.50 \text{ \AA}^{-1}$. The map was phased on all the atoms but only the contributions of the non-hydrogen atoms were actually subtracted. The peak heights of the hydrogen atoms ranged from 0.39 to 0.62 $e \text{ \AA}^{-3}$ and the largest spurious peaks in the map were +0.33 and -0.54 $e \text{ \AA}^{-3}$.*

* The following items have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30935 (50 pp., 1 microfiche): (a) a list of observed and calculated structure factors based on the parameters in Tables 2 and 3 (Supplement A); (b) a discussion of the quinone carbonyl bond lengths in which the values obtained in the present structure are compared with those reported in the literature and the need for a proper correction of many of these bond lengths for thermal motion is pointed out (Supplement B - Part I); (c) a table containing most of the dihedral angles between the planes defined in Table 5(a) and a figure illustrating the conformations of the BBQ groups in terms of the atomic deviations from planes (12) and (12') in Table 5(b) (Supplement B - Table 7 and Fig. 6); (d) a more detailed treatment of the analysis of thermal motion including a discussion of the orientations of the group translational and librational axes and of the individual thermal vibrational ellipsoids of the carbonyl oxygen atoms with respect to a group axial system based on the normals to the most, mean and least-squares planes (Supplement B - Part II, including Tables 8 and 9); and (e) a table containing the shortest intermolecular separations in the present structure and a figure showing the overlap for molecules of type I (Supplement B - Table 10 and Fig. 7). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Some of the preliminary calculations, namely the reduction and correlation of the film data, were done on a UNIVAC 1108 computer. The other calculations, including the application of Fourier methods and the least-squares refinement, were carried out on an XDS Sigma 7 computer.

Results and discussion

The values of the bond distances and bond angles in the two independent DFC molecules after correction for thermal motion are given in Figs. 1 and 2, respectively. Fig. 1 also shows the configurations of the molecules and the numbering scheme used in the subsequent discussion. The uncertainty in the correction for thermal motion has added approximately 0.001 Å to the e.s.d.'s in the lengths of the C–C and C–N bonds of the pyridyl groups given in Fig. 1 and approximately 0.004 Å to the e.s.d.'s in the C=O bond lengths. The least-squares derived e.s.d.'s in the bond angles are 0.2° for the C–O–C angles and range from 0.3 to 0.4° for the C–C–O, C–C–N, C–N–C and C–C–C angles. The corrections for thermal motion did not alter the values of the bond angles by more than 0.2° and the average change in the bond angles not involving hydrogen atoms was 0.03°. The corresponding experimental errors in the lengths and angles in which hydrogen atoms participate are estimated to be approximately 0.05 Å for C–H, N–H and O···H distances, 3° for H–C–C, H–N–C, and H–C–N angles and 4° for N–H···O and C–H···O angles.

Comparison of the corresponding bond distances in the two molecules shows that they are the same at the 5% confidence level (Cruickshank, 1959) since the ratio of the difference in bond length to the estimated standard deviation in that difference is less than 2 for all pairs of bond lengths. Similarly, all corresponding bond angles are the same at the 5% confidence level except the exocyclic angles C(10)–C(8)–O(9), C(10)–

C(8)–N(7) and C(8)–N(7)–C(4) for which the ratio of the difference in bond angle to the estimated standard deviation in that difference has values of 2.4, 2.4 and 3.6, respectively. These disparities in angle can be traced to the effect of distinctly different crystallographic environments on the molecular configuration of DFC.

Comparison with other structures

The values of the bond lengths and bond angles in the furan rings of the DFC molecules are intermediate between those reported in furan (Bak, Hansen & Rastrup-Andersen, 1955; Fourme, 1972) and in dibenzofuran (Dideberg, Dupont & André, 1972). The bond lengths and bond angles in the pyridyl group of the DFC molecules are very similar to those reported in other structures containing this group (Downie, Harrison, Raper & Hepworth, 1972). The somewhat higher values of the C–N–C angle and the correspondingly lower values of the average C–C–N angle in the structures of 2-(2-pyridylmethylthio)benzoic acid (Karle, Karle & Mitchell, 1969) and α -pyridoin (Ashida, Hirokawa & Okaya, 1965) apparently result from the participation of the pyridyl nitrogen atoms in strong O–H···N hydrogen bonding. The values of the bond angles and bond distances in the carboxamido groups are reasonable as the comparisons in Table 4 show. Interestingly enough, in those structures for which corrections to the C=O and C–N bond lengths for thermal motion have been made, these bond lengths are approximately related by the linear correlation $d_{C=O} = -d_{C=N} + 2.60$ Å, reflecting the variable contribution of the imino resonance form to the ground state of the carboxamido group.

The exocyclic C–N bond lengths of 1.420 and 1.422 Å in DFC molecules I and II, respectively, are typical of bonding between a nitrogen atom and an aromatic carbon atom when the nitrogen atom participates in the delocalized π system of the aromatic

Table 3. Fractional coordinates and isotropic temperature factors of the hydrogen atoms in DFC as derived from a final difference Fourier map

The isotropic temperature factors appearing in the table were deduced from the measured peak heights P by the expression $B = 2.25/P$. The mean errors are estimated to be 0.07 Å in the coordinates and 0.7 Å² in the temperature factors. The hydrogen atoms are numbered according to the heavier atoms to which they are linked.

	Molecule I				Molecule II			
	x/a	y/b	z/c	B (Å ²)	x/a	y/b	z/c	B (Å ²)
H(1)	–0.450	0.4595	–0.172	5.7	–0.576	–0.0010	–0.742	5.6
H(2)	–0.282	0.5800	–0.140	3.9	–0.580	0.0975	–0.648	4.0
H(3)	–0.105	0.6125	0.016	3.7	–0.386	0.1345	–0.511	3.8
H(6)	–0.420	0.3755	–0.025	4.1	–0.324	–0.0640	–0.675	4.4
H(7)	–0.075	0.4890	0.214	4.5	–0.038	0.0373	–0.403	4.5
H(11)	0.085	0.6820	0.360	4.6	0.047	0.2240	–0.229	4.3
H(13)	0.165	0.7455	0.526	4.6	0.220	0.2935	–0.088	4.4
H(14)	0.287	0.7507	0.695	3.8	0.384	0.3025	0.090	4.5
H(15)	0.359	0.6515	0.779	3.7	0.421	0.1938	0.169	5.4
H(16)	0.343	0.5538	0.683	3.8	0.341	0.0887	0.088	3.8
H(25)	0.433	0.3290	0.710	4.1	0.360	–0.1497	0.124	4.5
H(26)	0.435	0.2125	0.695	4.8	0.317	–0.2610	0.111	4.5
H(27)	0.318	0.1573	0.529	5.0	0.153	–0.3135	–0.039	4.5
H(28)	0.238	0.2300	0.390	4.7	0.040	–0.2535	–0.175	4.5

group. The exocyclic C–N–C angles, 128.3° in molecule I and 126.7° in molecule II, are enlarged as a result of the steric interaction between the carbonyl portion of

the carboxamido group and the pyridyl ring. A similar enlargement (to 127.6°) occurs in acetanilide (Brown, 1966). By contrast, the C–N–C angle is 119.6° in

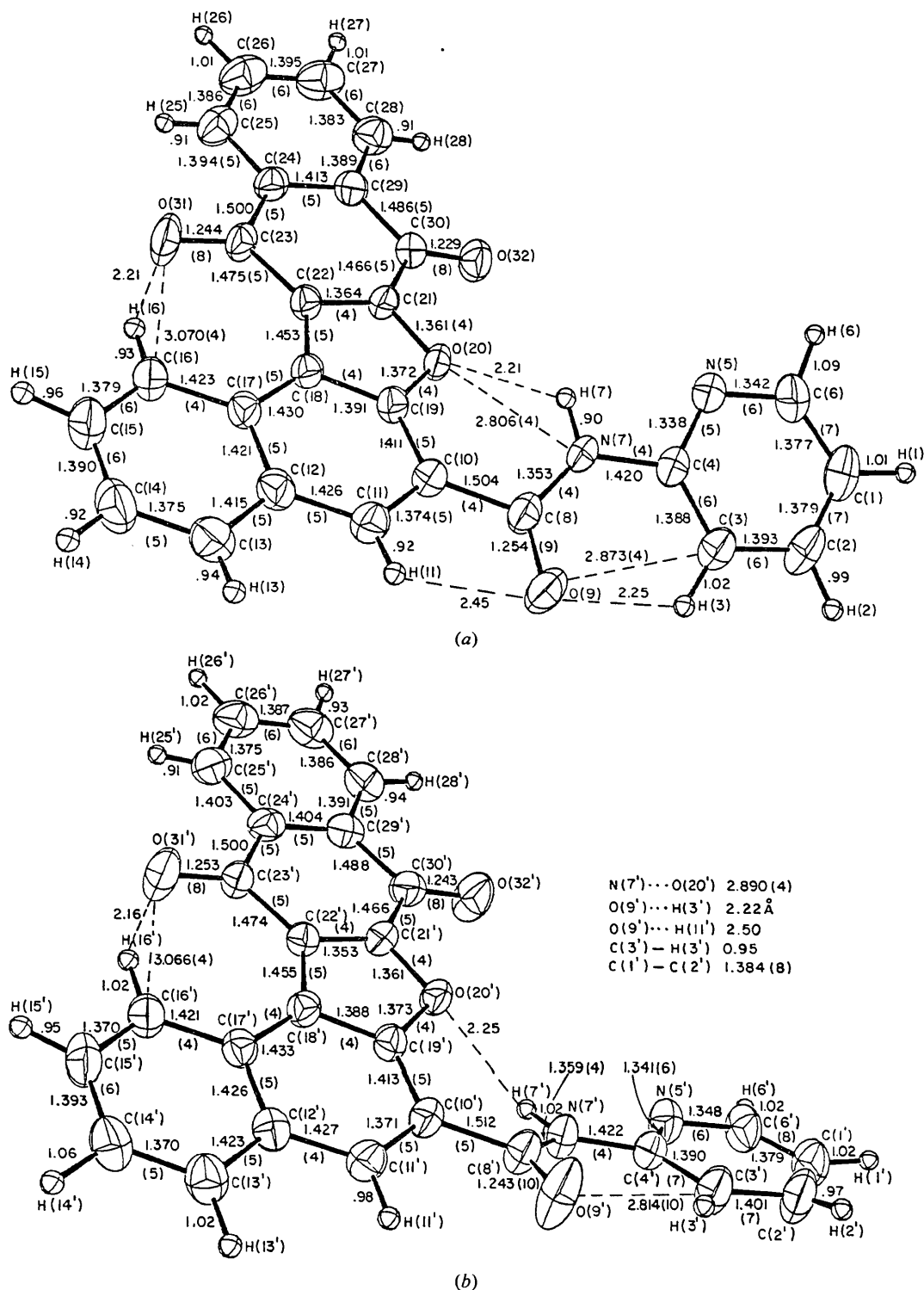


Fig. 1. ORTEP drawings of the two independent DFC molecules viewed at 28° from the least-squares normals of their respective BBQ ring systems. The bond distances (given in \AA) are accompanied by their least-squares derived e.s.d.'s (in parentheses). Individual thermal vibration ellipsoids are drawn at the 50% probability level. (a) Molecule I, (b) molecule II.

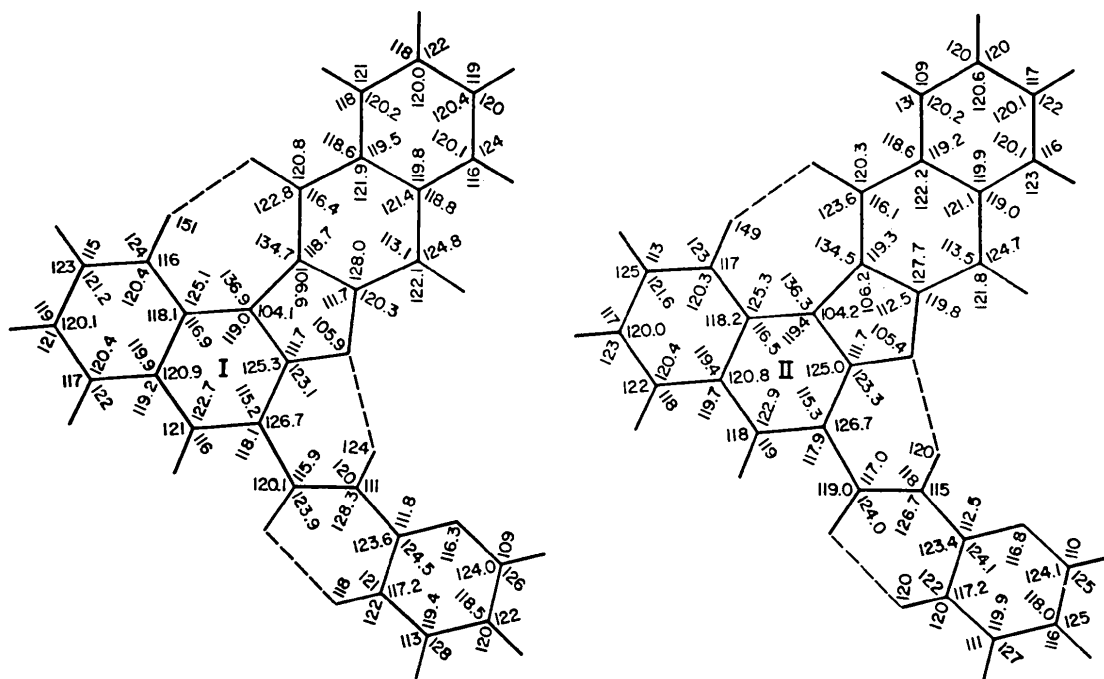


Fig. 2. Bond angles ($^{\circ}$) in DFC for molecule I (left) and molecule II (right).

Table 4. Bond distances (\AA) and bond angles ($^{\circ}$) in the carboxamido groups of DFC and of a number of other molecules

	C=O	C-N	C-C=O	N-C=O	C-C-N
DFCI	1.254*	1.353*	120.1	123.9	115.9
DFCII	1.243*	1.359*	119.0	124.0	117.0
<i>o</i> -ACAMI	1.25	1.35	120.7	123.6	115.7
<i>o</i> -ACAMII	1.27	1.32	118.5	122.7	118.7
<i>r</i> -ACAM	1.258*	1.338*	120.7	122.6	116.7
ACAN	1.219	1.354	121.6	123.1	115.3
NMeACAN	1.263*	1.344*	124.5	117.0	118.5
NMeTNACAN	1.230*	1.374*	122.9	120.6	116.5

o-ACAM = *o*-acetamide (Hamilton, 1965), *r*-ACAM = *r*-acetamide (Denne & Small, 1971), ACAN = acetanilide (Brown, 1966), NMeACAN = *N*-methylacetanilide (Pedersen, 1967), NMeTNACAN = *N*-methyl-2,4,6-trinitroacetanilide (Christoph & Fleischer, 1973).

* These values have been corrected for thermal motion.

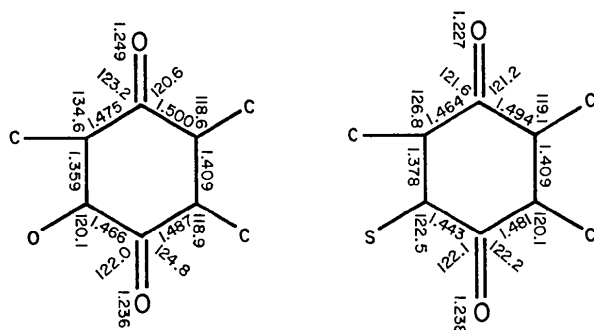


Fig. 3. Comparison of the average values of the bond lengths (\AA) and bond angles ($^{\circ}$) within the quinone ring between DFC (left) and NCNTD (right).

N-methylacetanilide (Pedersen, 1967), where the steric interaction between the ring and substituent is relieved by rotation of the phenyl group.

The average bond lengths and bond angles within the quinone ring of the DFC molecule compare very favorably with those found in 2-*N,N*-diethylamino-3-methoxycarbonylnaphtho[2,3-*b*]thiophene-4,9-dione, NCNTD (Gibbons, Lerscher & Trotter, 1972) which contains a thiophene ring fused to the quinone portion of a naphthoquinone ring system. Corresponding values are compared in Fig. 3. Analogous variations in the longer C-C bond lengths occur in many other aromatic quinones, for example in 5-methyl-1:2-benzanthraquinone (Ferrier & Iball, 1963*a*), and 2,5-dichloro-*p*-benzoquinone (Rees, 1970*b*). The large variations in the C-C-C angles, although more severe in the DFC molecules because of the perturbing effect of the neighboring furan ring, are also common to other quinones, as pointed out by Ammon, Sundaralingam & Stewart (1969). Moreover, one may note that variations in angle nearly identical with those in the quinone ring occur in the six-membered ring fused to the other side of the furan ring in the DFC molecules.

Molecular configuration

Although the two independent DFC molecules have approximately planar configurations, most of the groups composing each molecule deviate significantly from planarity. The equations of the best least-squares planes through various groups of atoms in each DFC molecule are given in Table 5(*a*) and the deviations of

atoms from some of these planes are given in Table 5(b) and (c) (Schomaker, Waser, Marsh & Bergman, 1959). Application of the χ^2 test (Stout & Jensen, 1968) indicates that only planes (1), (6) and (8') are truly planar [$P(\chi^2 > \chi_0^2) > 0.10$] whereas planes (3'), (6') and (12) are essentially planar ($P > 0.01$). The other planes deviate significantly from planarity ($P < 0.01$). The large deviations of atoms within the BBQ portions of the independent molecules from

planes (5) and (5') or (12) and (12') arise chiefly from the steric interaction between the quinone oxygen atom O(31) or O(31') and the hydrogen atom H(16) or H(16'). Analogous steric effects have been reported in other heteroaromatic systems containing quinone carbonyl groups, for example in 5-methyl- and 2'-methyl-1:2-benzanthraquinone (Ferrier & Iball, 1963a, b) and in the hydrazone derivative of 2,2'-di-(1,4-naphthoquinone) (Ammon & Gibson, 1970).

Table 5. Atomic deviations from various least-squares planes in DFC

(a) Equations of the best least-squares plane through various groups of atoms calculated by the method of Schomaker, Waser, Marsh & Bergman (1959) and given in terms of the coefficients *A*, *B*, *C* and *D* in the expression $AX + BY + CZ + D = 0$, where *X*, *Y*, *Z* are orthogonal coordinates in Å along axes *a*, *b* and *c**, respectively

Plane	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	Plane	Inclusive atoms
(1)	-0.92336	-0.32418	0.20570	0.8218		C(12)-C(17)
(2)	-0.91899	-0.32183	0.22777	0.6233	Naphthyl I	C(10)-C(19)
(3)	-0.94450	-0.23378	0.23081	-0.0169		C(24)-C(29)
(4)	-0.94366	-0.25492	0.21102	0.2482	Naphthoquinone I	C(21)-O(32)
(5)	-0.92700	-0.30689	0.21565	0.5407	BBQ I	C(10)-O(32)
(6)	-0.92587	0.17520	0.33476	-5.3614	Pyridyl I	C(1)-C(6)
(7)	-0.92531	0.17562	0.33609	-5.3625	N(pyridyl) I	C(1)-N(7)
(8)	-0.93958	0.00165	0.34231	-3.6352	Carboxamido I	N(7)-C(10)
(9)	-0.89604	-0.33987	0.28566	0.5698		
(10)	-0.91434	-0.32678	0.23916	0.6303		
(11)	-0.92624	0.00160	0.37692	-3.6803		C(4), N(7)-O(9)
(1')	-0.91634	-0.15269	0.37015	1.6992		C(12')-C(17')
(2')	-0.90481	-0.14924	0.39880	1.6650	Naphthyl II	C(10')-C(19')
(3')	-0.91511	-0.13750	0.37903	1.7737		C(24')-C(29')
(4')	-0.90598	-0.14523	0.39764	1.7316	Naphthoquinone II	C(21')-O(32')
(5')	-0.90197	-0.15617	0.40256	1.6913	BBQ II	C(10')-O(32')
(6')	-0.65469	-0.52210	0.54663	3.4615	Pyridyl II	C(1')-C(6')
(7')	-0.66143	-0.52628	0.53436	3.3520	N(pyridyl) II	C(1')-N(7')
(8')	-0.72164	-0.56523	0.39969	2.6140	Carboxamido II	N(7')-C(10')
(9')	-0.86577	-0.13833	0.48095	1.8504		
(10')	-0.89387	-0.15500	0.42069	1.7113		
(11')	-0.61032	-0.62144	0.49125	3.2516		C(4'), N(7'), C(8')
(12)	-0.91337	-0.32870	0.24024	0.6413	Furan I	C(18)-C(22)
(12')	-0.89053	-0.14325	0.43178	1.7176	Furan II	C(18')-C(22')

(b) Deviations (Å) of atoms from the least-squares planes associated with the BBQ portions of the DFC molecules

	(1)	(1')	(3)	(3')	(10)	(10')	(12)	(12')
C(8)	0.284	0.367					0.123	0.106
O(9)	0.014	0.905					-0.172	0.619
C(10)	0.133	0.163					0.027	0.002
C(11)	0.061	0.106					-0.025	0.002
C(12)	0.005	0.009					-0.030	0.001
C(13)	-0.003	-0.011					-0.020	0.036
C(14)	-0.001	0.002					0.031	0.141
C(15)	0.004	0.009					0.069	0.188
C(16)	-0.002	-0.010			0.050	0.069	0.046	0.119
C(17)	-0.002	0.001			0.001	0.003	-0.004	0.035
C(18)	0.018	0.029	0.289	0.111	-0.002	-0.006	-0.005	0.003
C(19)	0.079	0.112	0.328	0.182			0.006	-0.007
O(20)	0.083	0.172	0.203	0.218			-0.004	0.006
C(21)	0.047	0.094	0.106	0.137			0.002	-0.007
C(22)	0.007	0.019	0.150	0.082	0.002	0.006	0.002	0.003
C(23)			0.052	0.001	-0.001	-0.003	0.003	0.000
C(24)			0.009	-0.008			0.105	-0.007
C(25)			0.000	0.003			0.193	0.076
C(26)			-0.013	0.004			0.316	0.080
C(27)			0.016	-0.006			0.382	0.003
C(28)			-0.006	0.002			0.264	-0.062
C(29)			-0.006	0.005			0.129	-0.063
C(30)			-0.034	0.062			0.002	-0.085
O(31)			0.021	-0.044	-0.065	-0.006	-0.061	0.015
O(32)			-0.159	0.049			-0.098	-0.162
H(16)					0.10	0.13		
χ_0^2	4.52	27.1	30.8	10.1			9.2	16.0

Table 5 (cont.)

(c) Deviations (Å) of atoms from the least-squares planes associated with the pyridyl and carboxamido groups

	(6)	(6')	(8)	(8')	(9)	(9')	(11)	(11')
C(1)	0.003	0.001						
C(2)	-0.002	0.002						
C(3)	-0.003	-0.007					-0.218	-0.114
C(4)	0.005	0.009					0.001	0.000
N(5)	-0.003	-0.004						
C(6)	0.000	0.000						
N(7)	-0.007	0.071	0.004	-0.001	0.458	-0.530	-0.002	0.000
C(8)	0.180	0.230	-0.015	0.004	0.007	0.007	0.002	0.000
O(9)	0.392	0.181	0.004	-0.001	-0.330	0.494	-0.001	-0.166
C(10)			0.004	-0.001	-0.015	-0.015	0.077	0.201
C(11)			0.406	-0.495				
C(19)			-0.331	0.539	0.016	0.015		
O(20)					-0.006	-0.005		
H(3)							-0.45	-0.09
H(7)			0.13	-0.08	0.81	-0.98	0.14	0.07
χ^2	3.8	11.7	18.9	1.54				

The configurations of the two independent DFC molecules are characterized by the same general features, although the details vary somewhat because of differences in intermolecular environment.* Thus, the inclination of the pyridyl ring to the average plane of the BBQ system is 28.8° in molecule I and 26.9° in molecule II. However, the inclinations occur essentially in opposite directions, as can be seen in Fig. 1, and in the atomic deviations from planes (9) and (9') in Table 5(c). The relative orientation of the pyridyl group with respect to the BBQ portion can be expressed in terms of successive angular rotations from a coplanar configuration of the pyridyl, amido and carboxamido groups about the exocyclic C-N, N-C and C-C bonds. These angles are, respectively, 10.3, -2.1 and 19.2° in molecule I and 7.0, -8.9 and -25.8° in molecule II, negative values indicating counterclockwise rotations. These differences in the relative orientation of the pyridyl groups are caused by the participation of the N-H group in molecules of type II in an intermolecular hydrogen bond with the pyridyl nitrogen atom of a centrosymmetrically related molecule. Approximate coplanarity of the BBQ, carboxamido and pyridyl groups in each DFC molecule as revealed in the dihedral angles between any two of these planes and the relatively small torsion angles about the exocyclic bonds should be mentioned. Highly non-coplanar configurations have been observed in some analogous systems, notably in 2,2'-pyridil (Hirokawa & Ashida, 1961), where the planes of the picolinyl groups are rotated by 83° from one another about the bond joining them and in 1-phenyl-2-(2'-pyridyl)ethane-1,2-dione (Ashida, Hirokawa & Okaya, 1966), where the corresponding angle between the picolinyl and benzoyl groups is 88.1°. The molecular configurations observed in the present structure are sterically favored and are undoubtedly stabilized by intramolecular hydrogen bonding between the amino nitrogen atom and the furan oxygen atom. The

existence of intramolecular N-H...O hydrogen bonds has been well established in a number of structures such as α -pyridoin (Ashida & Hirokawa, 1965) and *N,N'*-diphenyl-1,8- and 1,5-diaminoanthraquinone (Bailey & Brown, 1967*a,b*), where N...O separations of 2.599, 2.578 and 2.602 Å respectively, have been reported. The observed intramolecular N...O separations in DFC, namely 2.806 Å in molecule I and 2.890 Å in molecule II, are larger than these but are still well within the range of N...O separations found in intermolecular N-H...O hydrogen bonds (Fuller, 1959). Further evidence is provided by the considerable increase in the N(7')...O(20') distance over the N(7)...O(20) distance and the consequent weakening of the intramolecular N-H...O hydrogen bond which accompanies the participation of the N-H group in molecule II in intermolecular N-H...N hydrogen-bond formation.

The tendency toward coplanarity in DFC molecules results in short intramolecular separations and large angular distortions. These distortions, for example C(16)-C(17)-C(18) > C(11)-C(12)-C(13), C(22)-C(23)-O(31) > C(24)-C(23)-O(31) and C(8)-C(10)-C(19) > C(8)-C(10)-C(11) can be readily traced to intramolecular steric factors. However, the nature of the C-H...O interactions which are associated with the short intramolecular C...O separations in the present structure merits further comment. Evidence of the repulsive character of the C(16)-H(16)...O(31) interaction in molecule I is found in the enlargement of the C(22)-C(23)-O(31) angle and in the large difference (14.4°) between the C(18)-C(22)-C(23) and O(20)-C(21)-C(20) angles. By contrast, the C-C-O angles in NCNTD (Gibbons *et al.*, 1972) are equal and the difference between the corresponding C-C-C and S-C-C angles is only 4.3°. This evidence is corroborated by the pattern of deviations of atoms C(16), H(16) and O(31) from plane (10). Similar arguments apply to the C(16')-H(16')-O(31') interaction in molecule II.

Although the C(3)...O(9) separation is short (2.873 Å), the pattern of deviations of atoms O(9),

* See footnote, part (c), on p. 2088.

C(3) and H(3) from plane (11) in Table 5(c) suggests that the C(3)–H(3)···O(9) interaction may also be steric in nature. On the other hand, the C(3')–H(3')···O(9') interaction in molecule II appears to be of the bonding type since the displacements of atoms C(3'), H(3') and O(9') from plane (11') have similar magnitudes and the same sign and the C(3')···O(9') distance is only 2.814 Å, considerably less than the C(3)···O(9) distance in molecule I and even less than the intramolecular C···O separations observed in a number of molecules where the C and O atoms are linked by only three interleaving bonds. These non-bonded C···O separations, for example, are 2.82 Å in picolinamide (Takano *et al.*, 1966), 2.84 Å in benzamide (Penfold & White, 1959), and 2.85 Å in acetanilide (Brown & Corbridge, 1954; Brown, 1966), and in the present structure, the comparable C(4)···O(9) and C(4')···O(9') distances are 2.931 and 2.906 Å, respectively. The angular distortions at atoms C(4'), N(7') and C(8') do not mar our argument since they can all be attributed solely to the non-bonding interactions between atoms C(3') and C(8') or C(4') and O(9'). Spectroscopic evidence for the participation of aromatic C–H bonds in intramolecular 'hydrogen' bonding has been presented by Berلمان (1969).

The out-of-plane distortions in the BBQ groups which stem from the intramolecular C–H···O interactions may be described in terms of the inclinations of the six-membered rings at the extremities of these groups from the planar central portions containing the furan rings [planes (12) and (12') in molecules I and II, respectively].* The average planes of these rings, defined in Table 5(a) by equations (1) and (3) for molecule I and (1') and (3') for molecule II, are tilted from the central portions by angles of 2.1, 5.8, 3.9, and 3.4°, respectively. Approximate directions for the axes of inclination may be deduced from the last two columns in Table 5(b). For planes (1) and (1') these axes are found to be approximately parallel to the C(13)–C(17) and C(13')–C(17') interatomic vectors, respectively, whereas for planes (3) and (3'), they are approximately parallel to the C(24)–C(29) and C(24')–C(27') vectors. The difference in orientation between the last two inclination axes can be shown to originate from the close intermolecular contacts between centrosymmetrically related quinone carbonyl groups of type II molecules, for example molecules IIB and IIG in Fig. 5, for which one finds intermolecular C···O and O···O separations of 3.33 and 3.31 Å, respectively, and a perpendicular separation between the bonds of 3.26 Å. The same interaction accounts for the observed difference in the deviations of atoms O(31) and O(31') from planes (10) and (10'), respectively, and for the different conformations of the quinone rings. These rings are boat-shaped in the two molecules but their vertices lie at atoms C(23) and C(30) in molecule I as opposed to atoms C(21') and C(24') in molecule II.

* See footnote, part (c), on p. 2088.

Since the bonds to the quinone carbonyl carbon atoms remain coplanar, the resultant relative orientations of the two carbonyl groups in each molecule also differ.

Thermal motion

When the thermal motion of the DFC molecules is analyzed by the method of Schomaker & Trueblood (1968) in terms of two rigid groups, one (BBQ) comprising the BBQ ring system without the quinone oxygen atoms but with atom C(8) and the other (NPyr) comprising the pyridyl ring with the attached N(7) atom, a reasonably good fit is obtained (r.m.s. ΔU_{ij} = 0.0023, 0.0027, 0.0014 and 0.0018 Å² for BBQI, BBQII, NPyrI and NPyrII, respectively).* The correction for librational motion increases the bond lengths within the NPyr groups by 0.004 to 0.008 Å (average 0.006 Å) in molecule I and by 0.004 to 0.010 Å (average 0.007 Å) in molecule II. The maximum value of the correction in the other non-carbonyl bonds is 0.003 Å and the mean value is 0.002 Å. The 'riding' model correction for the C=O bonds increases their lengths by 0.016 to 0.036 Å (0.030 Å average).

Packing arrangement

The two independent molecules are approximately planar and are arranged with their average planes approximately parallel to one another as shown in Fig. 4 to form sheets extending along the [010] and

* See footnote, part (d), on p. 2088.

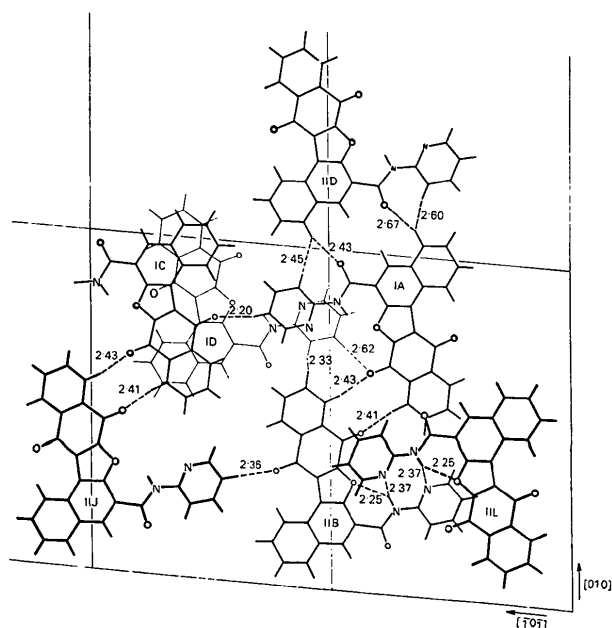


Fig. 4. Packing arrangement viewed along the normal to the mean molecular plane in the structure of DFC. The equivalent molecules have the following designation: If the reference molecule *A* is at x, y, z then *B* is at $-x, -y, -z$; *C* at $x-1, y, z-1$; *D* at $-x, 1-y, -z$; *J* at $-1-x, -y, -1-z$; and *L* at $x, y, 1+z$.

[101] directions. These sheets have a corrugated appearance because the molecules are slightly inclined to these directions. The angles formed with the [101] and [010] axes by the planes of the BBQ and pyridyl (Pyr) portions of the two independent molecules which lie in the same sheet are respectively 10.2 and 4.9° for

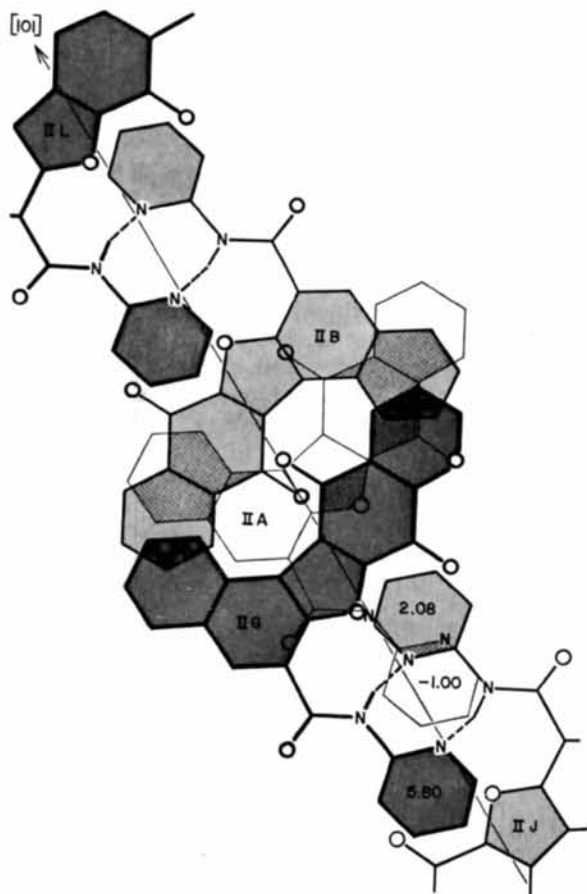


Fig. 5. Overlapping molecules of type II viewed along the normal to the mean molecular plane in DFC. The molecular labels are the same as those defined in Table 6.

BBQI, 0.2 and 3.1° for BBQII, 4.1 and 22.5° for PyrI and 13.8 and 20.9° for PyrII. Within a particular sheet the two independent molecules, for example IID and IA in Fig. 4 are related approximately by a twofold rotation about an axis parallel to the sheet normal. Intrasheet contacts are formed primarily by hydrogen atoms with hydrogen and oxygen atoms on adjacent molecules. The $H \cdots H$ distances are normal. However, five of the $H \cdots O$ distances are considerably shorter than 2.60 \AA , the sum of the van der Waals radii of the oxygen and hydrogen atoms (Pauling, 1960), and appear to be suitable candidates for $C-H \cdots O$ 'hydrogen bond' formation. The parameters for these 'bonds', namely $H \cdots O = 2.20, 2.36, 2.41, 2.43, 2.43 \text{ \AA}$; $C \cdots O = 3.197, 3.208, 3.227, 3.333, 3.346 \text{ \AA}$; and $C-H \cdots O = 168, 146, 149, 147, 166^\circ$ satisfy the geometrical and chemical criteria generally associated with hydrogen bonding (Fuller, 1959; Hamilton & Ibers, 1968). The predominance of geometrical over chemical criteria in determining whether a hydrogen bond is formed or not has been pointed out by Haslam & Eyring (1967) from their studies of D_2O solvent isotope effects on intramolecular hydrogen bonds. Additional evidence for the existence of such bonds has been presented by Sutor (1963) and other appropriate examples have been noted in the literature since then (Palenik, 1965; Ferguson & Islam, 1966; Rees, 1970a; Gaultier & Hauw, 1966). In the present structure, the $C-H \cdots O$ 'bonds' serve to link the molecules together into the observed sheet-like pattern. Five out of six carbonyl oxygen atoms participate in this network. Two atoms, namely O(31) and O(31'), join molecules of the same type, for example IC with IA and IIB with IIL, respectively, to form chains running along the [101] axis. Two others, O(32) and O(32'), join alternate chains together, for example via IIL to IC, to form double chains and the fifth atom, O(9), links the double chains together into sheets. The sixth carbonyl oxygen atom, O(9'), is too far from its neighboring hydrogen atoms to participate in intermolecular $C-H \cdots O$ 'hydrogen bonding'. However, as discussed earlier, it can participate instead in an intramolecular $C-H \cdots O$ 'hydrogen' bond.

Table 6. Parameters associated with overlapping π systems in the structure of DFC

GP1 and GP2 are the portions of the DFC molecules which directly overlap. MOL1 and MOL2 specify the particular molecules† to which groups GP1 and GP2 respectively belong. PLANE is the designation of the least-squares plane, as defined in Table 5(a), which best represents group GP1 and GP2. The equations of these planes were used to calculate the stacking angle,* the dihedral angle between groups GP1 and GP2 and d_{\perp} , the average interplanar separation between these groups. d_{min} is the minimum interatomic contact between groups GP1 and GP2 and TYPE is the nature of this contact. pyr = pyridyl, quin = naphthoquinone, naph = naphthyl.

GP1	MOL1	PLANE	GP2	MOL2	PLANE	Dihedral angle	d_{\perp}	d_{min}	TYPE	Stacking angle*
pyr	ID	(7)	pyr	IA	(7)	0°	3.40 \AA	3.447 \AA	$C \cdots N$	22.3°
pyr	IA	(6)	pyr	IK	(6)	0°	3.46	3.489	$C \cdots C$	22.2
quin	IE	(4)	naph	IA	(5)	3.1	3.35	3.374	$C \cdots C$	20.7
naph	IA	(2)	quin	IH	(5)	1.2	3.39	3.436	$C \cdots C$	22.6
naph	IIA	(2')	quin	IIB	(4')	0.2	3.40	3.375	$C \cdots C$	25.1
quin	IIB	(3')	naph	IIG	(1')	1.0	3.33	3.378	$C \cdots C$	23.7

* Angle between the stacking axis a and the normal to the average least-squares plane through the overlapping groups.

† The equivalent molecules have the following designation: If the reference molecule A is at x, y, z , then B is at $-x, -y, -z$; D at $-x, 1-y, -z$; E at $1-x, 1-y, 1-z$; G at $x-1, y, z$; H at $-x, 1-y, 1-z$; and K at $-1-x, 1-y, -z$.

Successive sheets are related by centers of symmetry lying midway between them. Some of the contacts between adjacent sheets involve hydrogen atoms and arise because of the large tilt of the pyridyl groups with respect to *b*. One of these contacts results in the formation of an intermolecular hydrogen bond between the amido and pyridyl nitrogen atoms on centrosymmetrically related type II molecules, for example IIB and IIL in Fig. 4, which links alternate sheets into double layers. The values of the N...N and H...N distances and of the N-H...N angle associated with this hydrogen bond are 3.254 Å, 2.37 Å and 145°, respectively. The N...N distance is rather long but is still within the range of reported intermolecular separations between hydrogen-bonded nitrogen atoms (Fuller, 1959; Hamilton & Ibers, 1968). The other contacts in which hydrogen atoms participate are normal. However, numerous short separations occur between C, N or O atoms of overlapping π systems both within and between the double layers. The nature of this overlap is illustrated in Fig. 5 for molecules of type II.

The complex pattern of overlapping regions can be described meaningfully in terms of contacts between three distinct portions of the DFC molecule, namely the naphthyl (naph), naphthoquinone (quin), and pyridyl (pyr) groups. Use of these groups to characterize the overlapping regions yields the information presented in Table 6. One may note, first, that of the many possibilities only two distinct types of overlap occur, namely naph over quin or *vice versa* and pyr over pyr, and second, that the overlap results in the formation of continuous stacks. The average planes of the overlapping groups are approximately parallel to one another and are separated by distances which vary from 3.33 to 3.46 Å. The angles between the normals to these planes and the stacking axis *a* are relatively small and very similar. All but one of the six independent groups in the DFC structure participate in both overlap and stacking. The sixth group, namely the pyridyl group of molecule II, participates in neither because the inclination of its normal to the stacking axis is too large (49.1°) and differs appreciably from the stacking angles formed by the other groups.

The separations between overlapping groups in the present structure are considerably smaller than the ones reported in other quinones whose structures are composed of stacks (Gaultier, Hauw & Breton-Lacombe, 1969). Slightly larger interplanar spacings are also observed in planar aromatic hydrocarbons classified as type *B* by Stevens (1962) on the basis of their fluorescence spectra. In these solids, molecular pairing or stacking normally leads to perpendicular interplanar separations ranging from 3.46 Å in α -perylene (Camerman & Trotter, 1964) and coronene (Fawcett & Trotter, 1965) to 3.53 Å in pyrene (Allmann, 1970). However, the stacking parameters in DFC do resemble those reported in weak π - π complexes where the contributions of the excited charge-

transfer states to the ground state of the complex are small or negligible (Prout & Wright, 1968). Analogous interactions can also occur between like aromatic molecules *via* π - π dispersion forces (Hirschfelder, Curtiss & Bird, 1954). In the present structure, these forces prevail over the weaker van der Waals forces and provide a suitable environment for the solid-state intermolecular energy transfer required to charge the pigment particles in the PEP mode (Förster, 1968; Birks & Kazzaz, 1968). On the other hand, a packing analysis of the structure of α -BBQ with the aid of PACK5 (Williams, 1969) showed that the overlap necessary for π - π dispersion interactions does not occur in that structure (Walker, Miller, Griffiths & Goldstein, 1972; Goldstein, 1974), the intermolecular interactions being dominated instead by van der Waals forces.

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